Volumetric and Viscometric Studies on the Long Chain fatty acid in Surfactant Stabilized Propanol

by
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January, 2015

Dedicated
To

My beloved Parents

Declaration

This is to certify that the thesis work entitled **"Volumetric and Viscometric Studies on the Long Chain fatty acid in Surfactant Stabilized Propanol"** has been carried out by Md. Abdus Salam 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.

29.1.15

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Abstract

Volumetric and viscometric studies of binary mixtures of (fatty acid + propanol) and ternary mixtures of (fatty acid + propanol + surfactant) were done. Lauric, palmitic and stearic acids were taken as fatty acids while the surfactant was sodium dodecyl sulfate (SDS). The investigated binary and ternary systems were carried out over a concentration range of 0.0100–0.4000 M of fatty acids at 298.15 to 323.15 K at 5 K intervals. The SDS concentrations were 0.001 M and 0.005 M.

The apparent molar volumes, φ_v of both binary and ternary mixtures were determined from the densities of the mixtures. The φ_v values have been found to be positive throughout the whole concentration range for all acids in propanol. The apparent molar volumes, φ_v of all fatty acids in propanol were found to be increased with concentration at all temperatures. Similarly φ_v values were found to be increased with increasing temperature at any concentration of the solution. These results may be due to the solute–solvent and solute–solute interaction in the solutions. This shows that φ_v values are strongly dependent upon concentration as well as the temperature. The φ_v values are also found to be increased with the chain length of the fatty acids and this may be due to the hydrophobic characters of alkyl chain. The number of carbon atoms in the hydrocarbon chain of the fatty acid is proportional to the degree of hydrophobic/hydrophilic balance of the whole compound. Eventually the pattern of apparent molar volumes of lauric, palmitic and stearic acids in 0.001 and 0.005 M SDS solution is very similar to those of (propanol + fatty acid) systems. The apparent molar volumes decreased at all concentration of SDS in comparison to corresponding systems without SDS. The results conferred that at molecular arrangements in SDS to (fatty acid+propanol) systems more organized than corresponding systems without SDS.

The values of viscosity (η) of lauric, palmitic, and stearic acids in propanol increased with concentration at all six temperatures. The increase of η values of all acids with concentration can be attributed to the increase in both solute–solvent and solute–solute interactions with concentration. At the same time, at a constant temperature and concentration, values of η are found to be increased with the carbon number along the hydrocarbon chain of the fatty acid

can be explained by the increase in both molecular mass of the fatty acid and the degree of solute–solvent interactions with carbon number. The ultimate pattern of viscosity after addition of SDS is almost similar to corresponding systems without SDS.

The change of free energy, ΔG and enthalpy, ΔH* values for viscous flow were found to be positive work had to be done to overcome the energy barrier for the flow process. The change of entropy, ΔS* values for the flow process are negative in all cases.

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Symbols / Abbreviations	**Explanation**
K_d	Dissociation Constant
λ_i	Ionic Conductance
η	Viscosity
λ_i^0	Limiting Ionic Conductance
A	Area of contact between the two layers
f	Tangential force
ϕ	Fluidity
l	length
Pa·s	Pascal-Second
mP	Millipoise
cP	Centipoise
mPa.s	Milli-Pascal-Second
v	Velocity
r	Radius
P	Pressure
t	Flow time
ρ	Density of the liquid/solution
h	difference in height of the surface of the two reservoirs
g	acceleration due to gravity
SDS	Sodium dodecyl sulfate
IUPAC	The International Union of Pure and Applied Chemistry

CHAPTER I

Introduction

1.1.1 The phenomena of solute-solvent interaction

Elucidation of the nature of ion-solvent interaction [1–2] and interpretation of the thermodynamic and transport processes in terms of such parameters as effective size of the solvated ions in solutions have been two of the most difficult problems in the understanding of electrolytic solutions. This is because there is not satisfactory model to represent the various phenomena that occur in solution and the incompleteness in the understanding of the structure of the liquids in general. There are a number of evidences of solvation of ions [1–2] or solute molecules a number of studies have discussed the effect of solvation on the equilibrium properties of liquids.

The process of solvation and the process of dissolution are known to be close related. When ionic crystal is added to a solvent, the electrostatic force of attraction between the oppositely charged ions in the crystal have to be overcome by interposing solvent layers around each of the ions. The ability of a solvent to dissolve a crystal is reflected by the following properties, its dielectric properties, polarity, degree of self-association and its ability to solvate. Studies on the phenomena of solvation have led to the conclusions that:

(i) The ionic compounds are moderately soluble in dipolar aprotic solvents of relatively high dielectric constant but are much more soluble in water and other hydroxylic solvents like methanol. A number of inorganic salts are dissociated in acetonitrile, which is otherwise known to solvate cations and anions rather poorly [3].

(ii) The dielectric constant alone is not an adequate measure of solvating ability and may even play a major role in determining the solvation of ionic species. Cations should be better solvated in solvents having atoms with an unshared electron pair like nitrogen and oxygen. The cations have been found to be strongly solvated in highly polar solvents with the negative charge localized on an oxygen atom, e.g. in sulphur dioxide, dimethyl sulfoxide, phosphorus oxide, dimethyl formamide [4]. Potassium iodide is less soluble than sodium iodide in methanol or water [5], but in dimethyl sulfoxide or dimethylformamide the reverse is true, which could be due to differences of cation solvation.

The anions have been found to be solvated in two ways:

(i) Small ions are mostly solvated by hydrogen bonding which is superimposed upon solvation by ion-dipole interactions, and

(ii) Large ions are solvated by interaction due to mutual polarizability of the anions and the solvent superimposed upon solvation by dipole interactions. Thus while the anions are more strongly solvated in hydrogen bonding solvents than in dipolar aprotic solvents, the cations are better solvated in the latter type of solvents.

The solubility of halides in various solvents generally follows the order:

Iodides > bromides > chlorides > fluorides.

The alkaline halides are more soluble in hydroxylic solvents than in the dipolar aprotic solvents like acetonitrile and acetone. These are found to be more soluble in acetonitrile than in acetone [6].Electrolytes may be divided into two categories: ionophores and ionogens. While the former are ionic in character in the crystalline state as well as in the fused state and in highly dilute solutions, the latter have molecular crystal lattice and ionize in solution only if suitable interaction occurs with the solvent molecules.

The ionophores may exist in solution as an equilibrium mixture containing ion-pairs and free ions [7].

$$\underset{\text{solvated}}{M^+X^-} \rightleftharpoons \underset{\text{solvated}}{M^+} + \underset{\text{solvated}}{X^-}$$

The ion-pairs are of oppositely charged ions having life terms sufficiently long to be recognized as kinetic entities in solution and in which only electrostatic forces are assumed

[1]. Fuoss *et al.* [8] have studied intensely the dependence of the dissociation constant, K_d, on the dielectric constant, the temperature and the nature of the salt. It was found to be large for solvents having high dielectric constant. It has also been found to be dependent on the distance of closest approach of the ions in the ion pairs. For hydroxylic solvents, large ions have larger K_d values and lower conductance values than smaller ions, which doesn't hold for other solvents.

Interaction of the ions with the solvent molecules causes low conductance. Na^+ ion behaves as a large ion as the K_d of iodides of Bu_4N^+ and Na^+ are found to be of the same order. Small ions like Li^+, F^- have low conductance in acetone [9] but have low K_d values which have been attributed to the loss of the solvent molecules from the ion-pairs [9].Solute-solvent interactions have been studied in details by various methods; some important ones may be listed as follows:

(i) Study of the solute-solvent interactions through transference experiments.
(ii) The effect of solvation on the ionic conductance.
(iii) The experiments applying stoke's law and their relevance to the nature of solvation.
(iv) Polarographic measurements of solutions.
(v) The spectral results due to the presence of the ions in solutions.

A relationship between the values of the limiting equivalent ionic conductance, λ_i and the viscosity, η value was advocated and utilized by Walden and others to study the solute-solvent interactions [10]. In one approach which assumes the constancy of the product $\lambda_1\eta$ the effects of variation of temperature, viscosity and variation of the solvent were studied. For large organic ions [10], the temperature co-efficient was found to be nearly constant in water as well as other non-aqueous solvents, while for the other ions it showed variations. For changing solvents, the product was found to vary widely in the case of inorganic ions which have been interpreted to be due to differences in solvation numbers of the ion in the various solvents. In another approach to this study Pure and Sherrington [11]used the relation between viscosity η_i, and limiting ionic conductance λ_1^0, to measure the radii of interaction of solvent and solute, called stoke's law radii, r. They compared the crystallographic radii of some cations and anions with stoke's law radii in the case of dimethylamide and dimethylsulphoxide solvents. They found the degree of solvation to decrease from lithium to cesium and to be less for silver and ammonium ions which have nearly comparable crystallographic radii. They postulated the anions to be unsolvated in dipolar aprotic solvents as the radii obtained are of the same order as that of the crystallographic radii, and that the negative end of the dipole in the solvent molecule is unshielded while the positive end is protected by two methyl groups, so that the cations, but not the anions are solvated by these solvents. Volumetric and viscometric measurement provides valuable tool for the determination of interaction among solutes and solvents.

1.1.2 Viscosity

Viscosity means viscous ability. Simply, viscosity of a material is resistance to flow. The internal friction which opposes the relative motion of the adjacent layers of a fluid causes for the resistance to flow. When a fluid is flowing through a cylindrical tube, 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.

Viscosity is really a frictional effect experienced by one layer of a liquid in moving past another in much the same way as an object experiences frictional resistance when dragged on a surface. The friction force, *f*, resisting the flow of one layer of fluid past the adjacent layer is proportional to the area, A, of the interface between the layers and to $\frac{du}{dr}$, the velocity gradient. This is Newton's lawand is given by

$$f = \eta A \frac{du}{dr}$$

where, η (eta, a Greek letter), the constant of proportionality, is called the *co-efficient of viscosity.* When the velocity gradient is unity and the area is 1 sq-cm, η is equal to the force; or the co-efficient of viscosity,η, may be defined as the force per 1 sq-cm required to maintain a difference of velocity of 1 cm per second between two parallel layers 1 cm apart. The reciprocal of the co-efficient of viscosity is known as the fluidity, ∅, or

$$\varnothing = \frac{1}{\eta}$$

Fluidity is a measure of the ease with which a liquid can flow. The connection between these quantities was first derived by J. L. M. Poiseuille in 1844, known as the Poiseuille equation [12]. 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 [12]:

$$\eta = \frac{\pi P r^4 t}{8 l v} \quad \ldots\ldots\ldots\ldots \quad (1.1.1)$$

This equation known as Poiseuille's equation holds accurately for stream-line flow but not for the turbulent flow which sets as higher velocities.

where, η is a proportionality constant, known as the coefficient of viscosity or simply viscosity of the liquid. The CGS 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. The SI unit of viscosity is the Pascal-second (Pa.S). Since viscosity of liquid is usually very small, it is usually expressed in millipoise (mP) or centipoise (cP) or mPa.S.

1.1.3 Factors affecting viscosity

Viscosity is first and foremost function of material. Most ordinary liquids have viscosities are in the order of 1 to 1000 mPa.S while gases have viscosities on the order of 1 to 10 µPa.S. Pastes, gels, emulsions, and other complex liquids are harder to summarize. Some fats like butter or margarine are so viscous that they seem more like soft solids than like flowing liquids.

Temperature: The viscosity of a simple liquid decreases with increasing temperature (and vice versa). As temperature increases, the average speed of the molecules in a liquid increases and the amount of time they spend "in contact" with their nearest neighbors decreases. Thus, as temperature increases, the average intermolecular forces decrease. The exact manner in which the two quantities vary is nonlinear and changes abruptly when the liquid changes phase.

Pressure: Viscosity is normally independent of pressure, but liquids under extreme pressure often experience an increase in viscosity. Since liquids are normally incompressible, an increase in pressure doesn't really bring the molecules significantly closer together. Simple models of molecular interactions won't work to explain this behavior and, to my knowledge, there is no generally accepted more complex model that does. The liquid phase is probably the least well understood of all the phases of matter.

While liquids get runnier as they get hotter, gases get thicker. The viscosity of gases increases as temperature increases and is approximately proportional to the square root of temperature. This is due to the increase in the frequency of intermolecular collisions at higher temperatures. Since most of the time the molecules in a gas are flying freely through the void, anything that increases the number of times one molecule is in contact with another will decrease the ability of the molecules as a whole to engage in the coordinated movement. The more these molecules collide with one another, the more disorganized their motion becomes.

Cohesive forces: Cohesive forces are the intermolecular forces (such as those from hydrogen bonding and van der Waals forces) which cause a tendency in liquids to resist separation. These attractive forces exist between molecules of the same substance. For instance, rain falls in droplets, rather than a fine mist, because water has strong cohesion which pulls its molecules tightly together, forming droplets. This force tends to unite molecules of a liquid, gathering them into relatively large clusters due to the molecules' dislike for its surrounding. The materials having stronger cohesive forces normally exhibit lower viscosities and vice-versa.

Adhesive force: Adhesive forces are the attractive forces between unlike molecules. They are caused by forces acting between two substances, such as mechanical forces (sticking together) and electrostatic forces (attraction due to opposing charges). In the case of a liquid wetting agent, adhesion causes the liquid to cling to the surface on which it rests. When water is poured on clean glass, it tends to spread, forming a thin, uniform film over the glasses surface. This is because the adhesive forces between water and glass are strong enough to pull the water molecules out of their spherical formation and hold them against the surface of the glass, thus avoiding the repulsion between like molecules. The materials having stronger adhesive forces normally reveal higher viscosities and vice-versa.

1.1.4 Properties of alcohol

In chemistry, an alcohol is any organic compound in which a hydroxyl group (–OH) is bound to a carbon atom of an alkyl or substituted alkyl group. It is composed of carbon, oxygen, and hydrogen and the general formula for a simple acyclic alcohol is $C_nH_{2n+1}OH$, where n=1, 2, 3, etc. The alkyl chain is often designated by the symbol R, so that ROH can represent any alcohol in the homologous series. The –OH group bonded to sp^3 hybridized carbon as shown above. It can therefore be regarded as a derivative of water, with an alkyl group replacing one of the hydrogen. The oxygen in an alcohol has a bond angle of around 109° (c.f. 104.5° in water), and two non-bonded electron pairs.

The properties of any given aliphatic alcohol depend on the nature of the alkyl group in the molecule and on the properties of the hydroxyl group. Generally, alcohols are clear, volatile and burn (oxidize) easily. Alcohols react with organic acids to form Esters. The reaction proceeds slowly but the rate of esterification is increased by the presence of hydrogen ions, which act as a catalyst in the reaction. Alcohols are very weak acids, intermediate in strength between acetylene and water. They undergo substitution with strongly electropositive metals such as sodium. Alcohols react with phosphorus pentachloride, when the hydroxyl group is replaced by a chlorine atom.

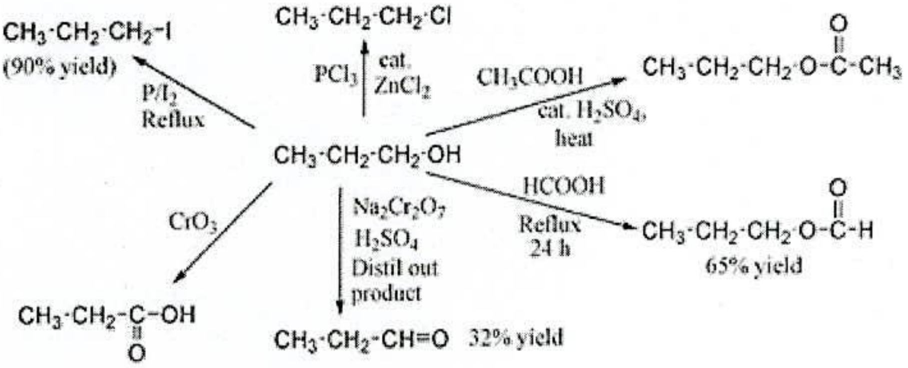
No gaseous alcohols are known at standard laboratory temperature. The lower members of the homologous series of aliphatic alcohols (containing C_1 to C_{10}) are clear colorless liquids at room temperature. They have varying solubility in water, the higher alcohols being less soluble. The alcohols higher than C_{12} are solids and are insoluble in water. Methanol, ethanol and propanol are miscible with water. The alcohols are miscible in all proportions with most organic liquids. The boiling points of the straight chain alcohols increase as the number of carbon atoms in the molecule increase. For a given molecular mass, there is a decrease in the boiling point when branching of carbon atoms occurs. Thus, the primary alcohols boil at a higher temperature than the secondary alcohols of the same molecular mass, and similarly, secondary alcohols have higher boiling points than the tertiary alcohols. The boiling points are much higher than is to be expected from their molecular masses. Hydrogen bonds alcohols associate neighboring molecules causes the boiling points high. These intermolecular bonds are considered to be intermediate in strength between weak van der Waals' forces and the strong forces between ions. The extra energy required to break the hydrogen bonds leads to an increase in boiling point.

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, propanol, etc. are all miscible with water. Alcohols with higher molecular masses tend to be less water-soluble, as the hydrocarbon part of the molecule, which is hydrophobic ("water-hating"), in nature. In this thesis 1-propanol has been used as solvent to find out the interaction of long chain fatty acids from the point of view of biological interests. The chemical formula of 1-propanol and some of its properties are listed in Table1.1.

Table 1.1: Some properties of 1-Propanol

Property	Data
Chemical Name	1-Propanol
Chemical formula	C_3H_7OH
Appearance	Colorless liquid
Molecular mass	60.10g mol^{-1}
Melting point	-126 °C
Boiling point	97-98 °C
Density	0.803 $g.cm^{-3}$
Viscosity	1.938 mPa.s (at 20°C)
Vapor pressure	1.99 kPa (at 20°C)
Solubility	Soluble in water

1-Propanol shows the normal reactions of a primary alcohol. Thus it can be converted to alkyl halides; for example red phosphorus and iodine produce *n*-propyl iodide in 80% yield, while PCl_3 with catalytic $ZnCl_2$ gives 1-chloropropane. Reaction with acetic acid in the presence of an H_2SO_4 catalyst under Fischer esterification conditions gives propyl acetate, while refluxing propanol overnight with formic acid alone can produce propyl formate in 65% yield. Oxidation of 1-propanol with $Na_2Cr_2O_7$ and H_2SO_4 gives only a 36% yield of propanaldehyde and oxidation with chromic acid yields propanoic acid. In short, some common reactions of propanol:



1-Propanol is thought to be similar to ethanol in its effects on human body, but 2-4 times more potent.

1.1.5 Surfactant

Surfactants are compounds that lower the surface tension of a liquid, the interfacial tension between two liquids, or that between a liquid and a solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents, dispersants and applications such as cleaning, cosmetics, environmental remediation, etc.

Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic groups (tails) and hydrophilic groups (heads). Therefore, a surfactant molecule contains both a water insoluble (oil soluble) component and a water soluble component. Surfactant molecules will migrate to the water surface, where the insoluble hydrophobic group may extend out of the bulk water phase, either into the air or, if water is mixed with oil, into the oil phase, while the water soluble head group remains in the water phase. This alignment and aggregation of surfactant molecules at the surface acts to alter the surface properties of water at the water/air or water/oil interface. Because air is not hydrophilic, surfactants are also foaming agents to varying degrees. Completely non-polar solvents known as degreasers can also remove hydrophobic contaminants, but lacking polar elements may not dissolve in water.

Surfactants reduce the surface tension of water by adsorbing at the liquid-gas interface. They also reduce the interfacial tension their tails form a core that can encapsulate an oil droplet, and their (ionic/polar) heads form an outer shell that maintains favorable contact with water. When surfactants assemble in oil, the aggregate is referred to as a reverse micelle. In a reverse micelle, the heads are in the core and the tails maintain favorable contact with oil.

Surfactants are classified into four primary groups; anionic, cationic, non-ionic, and zwitterionic (dual charge). Thermodynamics of the surfactant systems are of great importance, theoretically and practically. This is because surfactant systems represent systems between ordered and disordered states of matter. Surfactant solutions may contain an ordered phase (micelles) and a disordered phase (free surfactant molecules and/or ions in the solution). They have a vital role to play insulation of highly surface-active materials exhibit unusual physical properties. In dilute solution the surfactant acts as a normal solute. At fairly well defined concentrations, however an abrupt change in several physico-chemical properties such as viscosity, osmotic pressure, turbidity, electrical conductance and surface tension take place. The change of viscosity of a solution in presence of surfactant is quite interesting. In this research sodium dodecyl sulfate (SDS) has been used to find out the change of several physico-chemical properties of the investigated solutions. The chemical formula of SDS is given below and some of its physical and chemical properties are shown Figure 1.1 and Table 1.2.

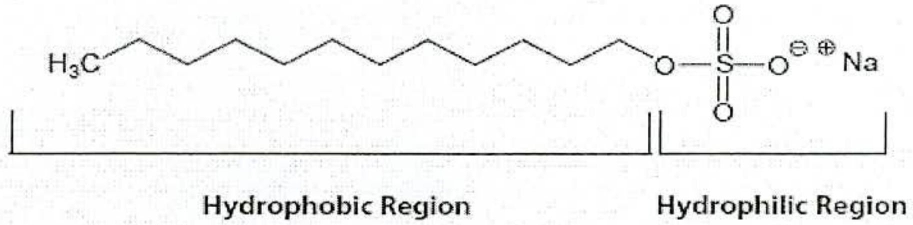


Figure 1.1: Structural formula of Sodium dodecyl sulfate showing hydrophobic and hydrophilic region

Table 1.2: Some properties of Sodium dodecyl sulfate

Property	Data
Chemical Name	Sodium dodecyl sulfate (SDS)
Chemical formula	$C_{12}H_{25}OSO_3Na$
Appearance	White crystalline powder
Molecular mass	288.38g.mol^{-1}
Detergent Class	Anionic
Melting point	206°C
Density	1.01 g.cm^{-3}
Specific gravity	0.4
Solubility	Soluble in water 250 g.L^{-1} at 20 °C
pH	5 to 8

1.1.6 Lauric Acid

Lauric acid, also called dodecanoic acid is a common saturated fatty acid with the molecular formula $CH_3(CH_2)_{10}COOH$. Molar mass of acid is 200.32 and density is 0.8801 g/cm^3. The melting point and boiling point of lauric acid are 43.2 °C and 298.9 °C respectively. It is the main acid in coconut oil and in palm kernel oil, and is believed to have antimicrobial properties. It is a white, powder solid with a faint odor of bay oil or soap. Lauric acid is inexpensive, has a long shelf-life, and is non-toxic and safe to handle. Thus, it is often used in laboratory investigations of freezing-point depression. It is a solid at room temperature but melts easily in boiling water, so liquid lauric acid can be treated with various solutes and used to determine their molecular masses. Lauric acid, although slightly irritating to mucous membranes, has a very low toxicity and so is used in many soaps and shampoos. Sodium lauryl sulfate is the most common lauric acid derived compound used for this purpose. Because lauric acid has a non-polar hydrocarbon tail and a polar carboxylic acid head, it can interact with polar solvents (the most important being water) as well as fats, allowing water to dissolve fats. This accounts for the abilities of shampoos to remove grease from hair. Fatty acids are a carboxylic acid with a long unbranched aliphatic tail (chain), which is either saturated or unsaturated. Fatty acids derived from natural fats and oils may be assumed to have at least 8 carbon atoms. Most of the natural fatty acids have an even number of carbon atoms, because their biosynthesis involves acetyl-CoA, a coenzyme carrying a two-carbon-atom group [13–14].Different physico-chemical properties of lauric acid in solution may provide important information in biological, pharmaceutical and many other systems. The apparent molar volumes, the apparent molar expansivities, the viscosities of lauric acid in proanol and in surfactant assorted propanol to understand the solution behavior are interest of this study, which are of industrial and biochemical importance.

1.1.7 Palmitic acid

Molecular formula of palmitic acid is $CH_3(CH_2)_{14}COOH$. Its nomenclature according to IUPAC, is hexadecanoic acid. Molar mass of acid is 256.42 and density is 0.853 g/cm^3. The melting point of Palmitic acid is 62.9 °C and boiling point of palmitic acid is 351-352 °C at 100mmHg.Palmitic acid is one of the most common saturated fatty acids found in animals and plants. As its name indicates, it is a major component of the oil from palm trees (palm oil and palm kernel oil). Palmitic acid is the first fatty acid produced during lipogenesis (fatty acid synthesis) and from which longer fatty acids can be produced. Palmitic acid is a fatty acid, a type of carboxylic acid which has a long aliphatic tail, which is unbranched and either saturated or unsaturated. If fatty acids are derived from natural fats or oils, they will have at least 8 carbon atoms. Most fatty acids derived from natural sources have an even number of atoms of carbon. The most common palmitic acid sources are the oils from palm trees, like palm oil, coconut oil and palm kernel oil. As mentioned earlier, the name for the fatty acid is derived from the French term for the pith (substance found in vascular plants) of the palm tree. Butter, milk, meat and cheese are also good sources of palmitic acid.

The most widely known use of palmitic acid is that it is an essential ingredient in soap making. During the Second World War, palmitic acid was used after being combined with naphtha, the most volatile part of liquid hydrocarbons, to form napalm, which is a gelling agent that is used in defense operations. About the intake of palmitic acid, researchers are still debating over its effects. According to the World Health Organization, consumption of palmitic acid can increase the chances of occurrence of cardiovascular diseases. There is a contradictory study that says, intake of palmitic acid has no such effect. Palmitic acid derivatives are used in different anti-psychotic medicines, especially in the treatment of schizophrenia. Different physico-chemical properties of palmitic acid in solution may provide important evidence in biological, pharmaceutical and many other systems. The apparent molar volumes, the apparent molar expansivities, the viscosities of palmitic acid in propanol and in surfactant assorted propanol to comprehend the solution behavior are concern of this thesis, which are of industrial and biochemical importance.

1.1.8 Stearic acid

Stearic acid is one of the saturated fatty acid with the formal IUPAC name octadecanoic acid. Its name comes from the Greek word stéar (genitive:stéatos), which means tallow. It is a waxy solid, and chemical formula is $CH_3(CH_2)_{16}COOH$. Molar mass of stearic acid is 284.48and density is 0.847 g/cm^3 at 70 °C. Melting point and boiling point of stearic acid are 70 °C and 383 °C respectively. Stearic acid occurs in many animal and vegetable fats and oils, but it is more common in animal fat than vegetable fat. The important exceptions are cocoa butter and shea butter whose fatty acids consist of 28–45% stearic acid[16].Stearic acid is prepared by treating animal fat with water at a high pressure and temperature, leading to the hydrolysis of triglycerides. It can also be obtained from the hydrogenation of some unsaturated vegetable oils. Stearic acid undergoes the typical reactions of saturated carboxylic acids, notably reduction to stearyl alcohol, and esterification with a range of alcohols. They are heated and mixed with caustic potash or caustic soda.

Stearic acid is useful as an ingredient in making candles, plastics, dietary supplements, oil pastels and for softening rubber [17]. It is used to harden soaps, particularly those made with vegetable oil. Stearic acid is also used as a parting compound when making plaster castings from a plaster piece mold or waste mold and when making the mold from shellacked clay original. In this use, powdered stearic acid is dissolved in water and the solution is brushed onto the surface to be parted after casting. This reacts with the calcium in the plaster to form a thin layer of calcium stearate which functions as a release agent. Esters of stearic acid with ethylene glycol, glycol stearate and glycol di-stearate, are used to produce a pearly effect in shampoos, soaps, and other cosmetic products. It is used along with simple sugar or corn syrup as a hardener in candies. It is used with zinc as zinc stearate as fanning powder for cards to deliver smooth fanning motion. Stearic acid is one of the most commonly used lubricants during injection molding and pressing of ceramic powders [18].Stearic acid is less likely to be incorporated into cholesterol esters. In epidemiologic and clinical studies stearic acid is associated with low density lipoprotein; lowered cholesterol in comparison with other saturated fatty acids [19].These findings may indicate that stearic acid is less unhealthy than other saturated fatty acids. Different physico-chemical properties of stearic acid in solution may provide important evidence in biological, pharmaceutical and many other systems. The apparent molar volumes, the apparent molar expansivities, the viscosities of stearic acid in propanol and in surfactant assorted propanol to comprehend the solution behavior are concern of this thesis, which are of industrial and biochemical importance.

Theoretical Background

1.2.1 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 inter atomic 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 mass 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 [20].

(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 7.8while in ketonic group (=CO) it is 12.2.The molar refraction, molecular viscosity etc. are the other examples 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.

1.2.2 Molarity

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

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

$$or\ C = \frac{n}{V} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1.2.1)$$

The unit of molarity is $mol.L^{-1}$.

1.2.3 Molar volume of Mixtures

The volume in mL occupied by 1 mole of any substance is called the molar volume. On the other hand, if ρ is the density and M be the molar mass, molality (m) of a solution is defined as the number of moles of the solute per 1000 g of solvent. Mathematically,

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

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

$$\text{or, } \mathrm{m} = \frac{\mathrm{a}}{\mathrm{M_2}} \times \frac{1000}{\mathrm{V_1} \times \rho_0} \cdots\cdots\cdots (1.2.2)$$

Where, a = weight of solute in gram

M_2 = molecular mass of solute in gram

V_1 = volume of solvent in mL

ρ_0 = density of solvent in g.cm^{-3}

$$\text{Specific volume, (V)} = \frac{1}{\rho} mLg^{-1} \cdots\cdots\cdots (1.2.3)$$

$$\text{Molar volume, } (\mathrm{V_m}) = \frac{M}{\rho} mLmol^{-1} \cdots\cdots\cdots (1.2.4)$$

When two components are mixed together, there may be either a positive or a negative deviation in volume. One of cause of positive deviation in volume i.e. volume expansion has been explained by the disruption of the mode of association through H–bonding of liquids. The negative deviation in molar volume i.e. volume contraction has been thought of by many observers, as arising from:

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.

1.2.4 Apparent molar volume

The apparent molar volume of a solute in solution, generally denoted by φ_v and is defined by the relation [21]

$$\varphi_v = \frac{V - n_1\overline{V}_1^0}{n_2} \quad \text{(1.2.5)}$$

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 molar volume of the pure solvent at specified temperature and pressure. For binary solution, the apparent molar volume (φ_v) of an electrolyte in an aqueous solution is given by [22],

$$\varphi_v = \frac{1}{n_2}\left[\frac{n_1M_1 + n_2M_2}{\rho} - n_1\overline{V}_1^0\right] \quad \text{(1.2.6)}$$

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

n_1 and n_2 are the number of moles, M_1 and M_2 are molar masses of the solvent and solute respectively and ρ is the density of the solution. For molar concentration, $n_2 = m$, the molality and n_1, the number of moles of solvent in 1000g of solvent, the equation for apparent molar volume takes the form [22, 23],

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

$$\text{or, } \varphi_v = \left[\frac{M_2}{\rho} - \frac{1000(\rho - \rho_0)}{m\rho\rho_0}\right] \quad \text{(1.2.7)}$$

$$\text{or, } \varphi_v = \frac{1}{\rho}\left[M_2 - \frac{1000}{m}\left(\frac{W - W_0}{W_0 - W_e}\right)\right] \quad \text{(1.2.8)}$$

where, ρ_o and ρ are the densities of the solvent and solution and W_e, W_o and W are the weight of empty specific gravity bottle (pycnometer), weight of pycnometer with solvent and weight of pycnometer with solution respectively.

If the concentration is expressed in molarity (C), the equation (1.2.7) takes the form [24]:

$$\varphi_v = \left[\frac{M_2}{\rho_0} - \frac{1000(\rho - \rho_0)}{C\rho_0}\right] \quad \text{(1.2.9)}$$

where, the relation, $C = \dfrac{m.\varphi_v.1000}{1000 + \varphi_v.m.\rho_0}$ is used for inter conversion of the concentration in the two scales [24].

The partial molar 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 molar 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:

$$\overline{Y_1} = \left(\frac{\delta Y}{\delta n_1}\right)_{n_2,P,T} \quad \text{(1.2.10)}$$

Similarly for component 2,

$$\overline{Y_2} = \left(\frac{\delta Y}{\delta n_2}\right)_{n_1,P,T} \quad \text{(1.2.11)}$$

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,

$$Y_{(n_1,n_2)} = n_1\overline{Y_1} + n_2\overline{Y_2} \text{ at constant T and P} \quad \text{(1.2.12)}$$

In respect of the volume of solution, equation 1.2.5 gives directly

$$V = n_1\overline{V_1} + n_2\overline{V_2} \text{ at constant T and P} \quad \text{(1.2.13)}$$

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

The concentration dependence of the apparent molar volume of electrolytes have been described by the Masson equation [25], the Redlich-Mayer equation [27] and Owen-Brinkley equation [26]. Masson [25] found that the apparent molar volume of the electrolytes vary with the square root of the molar concentration as,

$$\varphi_v = \varphi_v^0 + S_v\sqrt{c} \quad \cdots \quad (1.2.14)$$

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

Redlich and Rosenfeld [27] predicated that a constant limiting law 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,

$$S_v = KW^{3/2} \quad \cdots \quad (1.2.15)$$

where, the terms K and W are given by

$$K = N^2e^3\left(\frac{8\pi}{100D^3RT}\right)^{1/2}\left\{\left(\frac{\delta \ln D}{\delta\rho}\right)-\left(\frac{\beta}{3}\right)\right\} \quad \cdots \quad (1.2.16)$$

and $$W = 0.5\sum \gamma_i Z_i^2 \quad \cdots \quad (1.2.17)$$

where, β is the compressibility of the solvent, γ_i is the number of ions of the species i of valency Z_i formed by one molecule of the electrolyte and the other symbols have their usual significance [27].For dilute solutions the limiting law for the concentration dependence of the apparent molar volume of electrolytes is given by the equation,

$$\varphi_v = \varphi_v^0 + KW^{3/2}\sqrt{C} \quad \cdots \quad (1.2.18)$$

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

$$\varphi_v = \varphi_v^0 + S_v\sqrt{C} + b_vC \quad \cdots \quad (1.2.19)$$

where, S_v, is the theoretical limiting law slope and b_v an empirical constant.

1.2.5 Viscosity

Viscosity means viscous ability. The internal friction 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 center of the tube, the layer in the center of the tube having the maximum velocity. There thus exists a velocity gradient. 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 $$f = \eta A \frac{dv}{dx} \quad \text{……………………………} \quad (1.2.20)$$

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.

$$\phi = \frac{1}{\eta} \quad \text{……………………………} \quad (1.2.21)$$

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 according to J. L. M. Poiseuille [28]:

$$\eta = \frac{\pi \Pr^4 t}{8lv} \quad \text{……………………………} \quad (1.2.22)$$

This equation known as Poiseuille's holds accurately for stream-line flow but not for the turbulent flow which sets as higher velocities. After correction for kinetic energy, the equation becomes,

$$\eta = \frac{\pi \Pr^4 t}{8lv} - \frac{\rho V}{8\pi lt} \quad \text{……………………………} \quad (1.2.23)$$

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

The driving pressure P = $h\rho g$, 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 (1.2.23) becomes,

$$\eta = \frac{\pi h \rho g r^4 t}{8vl} \quad \text{(1.2.24)}$$

For a particular viscometer h, l, r and v are fixed, so the equation (1.2.24) becomes,

$$\eta = A\rho t \quad \text{(1.2.25)}$$

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

Putting the values of A, ρ and t of the investigated liquid in equation (1.2.25), the coefficient of viscosity can be obtained for a liquid at a definite temperature.

The CGS Unit of viscosity is poise, in honor of J.L.M. Poiseuille. The SI unit of viscosity is the pascal-second (Pa.S). Since viscosity of liquid is usually very small, it is usually expressed in centipoise (cP) or mPa.S.

1.2.6 Different thermodynamic parameters

Eyring and co-workers [29] using absolute reaction rate theory and partition functions corrected viscosity, η as follows:

$$\eta = \frac{hN}{V_m} e^{\frac{\Delta G^*}{RT}} \quad \text{(1.2.26)}$$

where, ΔG^* is the change of free energy of activation per mol for viscous flow, V_m is the molar volume for pure liquids or solutions and h, N, R and T have usual meaning. The values of change of free energy of activation (ΔG^*) can be calculated by using the Nightingle and Benck equation [30],

$$\varDelta G^{*} = RTln\left(\frac{\eta V_m}{Nh}\right) \qquad (1.2.27)$$

The experimental term in equation 1.2.29 depends on the temperature and is typical for the processes which require activation energy. The activation process to which ΔG* refers cannot be precisely described but in general terms, it corresponds to passes of the system into some relatively favorable configuration, from which it can then easily go to the final state of the molecular process.

Values for the corresponding thermodynamic parameters, enthalpy of activation, ΔH^{*} and entropy of activation ΔS^{*} for per mol for viscous flow of the liquids or solutions have been calculated from the relationship (1.2.28).

$$ln\frac{\eta V}{hN} = \frac{\Delta H^{*}}{RT} - \frac{\Delta S^{*}}{R} \qquad (1.2.28)$$

Assuming $\boldsymbol{\Delta H^{*}}$and $\boldsymbol{\Delta S^{*}}$to be almost independent in the temperature range studied, a plot of $\mathbf{ln}\frac{\boldsymbol{\eta V_m}}{\boldsymbol{Nh}}$ against $\frac{\mathbf{1}}{\boldsymbol{T}}$ will give a straight line. From the slope and intercept $\mathbf{\Delta H^{*}}$and $\mathbf{\Delta S^{*}}$ can be determined respectively.

CHAPTER II

Literature Review

2.1 Literature Review

Viscometric facts make available important information in fuel and hydrocarbon based industry. Viscosities and densities are two of the main properties evaluated which will depend on the raw materials used on the biodiesel fuel production [31]. Density data are relevant because injection systems, pumps and injectors must deliver the amount of fuel precisely adjusted to provide proper combustion [32]. Boudy and Seers show that fuel density is the main property that influences the amount of mass injected [33]. The viscosity is required not only for the design of pipes, fittings, and equipment to be used in industry of oil and fuel [34, 35] but also for monitoring the quality of fuel itself to be used in diesel engines. A viscous fuel, causing a poorer atomization, which is the first step of combustion, is responsible for premature injector cooking and poor fuel combustion [34, 36]. Many studies have been devoted to the measurement and prediction of the density and viscosity of biodiesel fuel as a function of temperature.

Several models have been proposed in the literature to calculate biodiesel fuel density. The most important among them rely on the accurate knowledge of the properties of the pure compounds. Tat and Van Gerpen [35] and Clements [36] used a linear mixing rule of pure densities based on the empirical equation. Huberet *al.,* [37] also uses density mixing rule to develop preliminary thermodynamic model for biodiesel fuel. Similarly, for the viscosities the approaches proposed by Krisnangkura *et al.* [38] and Yuan et al. [39] allow the estimation of the viscosity of biodiesel fuel using the Grunberg-Nissan equation that requires accurate values of the viscosities of pure Fatty Acid Methyl Esters or Fatty Acid Ethyl Esters [42].

Information about transport properties such as the viscosity of liquids is essential for the design of pipes, accessories, and equipment utilized in the oil and fat industry. These properties affect flow characteristics, loss of energy due to friction, mass, and heat transfer coefficients among other important variables [43–45]. Much work has been done on measuring and estimating transport properties of fatty compounds and vegetable oils as a function of temperature [46–52]. In most cases, specific equations were generated by adjusting each set of experimental data to a specific compound or to a class of compounds. More generalized models were developed for fatty acids [47, 51], triacylglycerols [47] fattyesters [51] and edible oils[46–48, 50].

Members of fatty acids with a small number of carbons in the chain may have slight solubilities in water but the solubility diminishes as the number of carbons in the chain increases. Triglycerides are much less soluble in water as they have a very small hydrophilic portion in their molecular structures. On the other hand, the solution behavior of such compounds can be investigated in a systematic manner in non-aqueous solvents with less or no polarity in which these compounds are more soluble [53, 54]. Such investigations in non-aqueous solvents may help estimate at least the trends in interactions of fatty acids or triglycerides with water. Viscosities, apparent molar volumes, expansivities and is entropic compressibilities are important tools to study solute-solvent interactions as well as reactions. Activation and reaction volumes have been extensively reviewed by Drljaca et al. [53]. Earlier reviews by Millero [54, 55] are important key references in studying solute-solvent interactions via the apparent molar volumes. The above properties have proven to be sensitive to revealing information on the solute-solvent interactions for various solutes by earlier work. The solution behavior of compounds with asymmetric carbon atoms [56] in amino acids in water and in guanidine hydrochloride, in relation to denaturation [57] of proteins and their denaturation in urea [58, 59] and ionic hydration volumes in relation to solution properties and ionic adsorption [60] were successfully studied by one or more of the above methods.

Recently, increasing attention has been devoted to the studies of the effects of the organic additives, on the micellization processes in the non-aqueous solutions [61–64]. Especially, increasing interest is being concentrated on the studies of the incorporation or solubilization of alcohols, which play a very important role in the preparation of micro emulsions [65–67]. Polar organic solvents resembling water in properties, such as ethylene glycol, glycerol, formamide and N, N-dimethyl acetamide, have been widely investigated. These solvents share three physical properties [68]: (i) high cohesive energy, (ii) high dielectric constant, and (iii) hydrogen bonding. However, it has been proposed that the ability for a solvent to form hydrogen bonds is the key condition for micellization [69].

The basic structure, a hydrophobic hydrocarbon chain with a hydrophilic polar group at one end, endows fatty acids and their derivatives with distinctive properties, reflected in both their food and industrial use. Saturated fatty acids have a straight hydrocarbon chain. A trans-double bond is accommodated with little change in shape, but a cis bond introduces a pronounced bend in the chain. In the solid phase, fatty acids and related compounds pack with the hydrocarbon chains aligned and, usually, the polar groups together. The details of the packing, such as the unit cell angles and head-to-tail or head-to-head arrangement depend on the fatty acid structure

The melting point increases with chain length and decreases with increasing saturation. Among saturated acids, odd chain acids are lower melting than adjacent even chain acids. The presence of cis-double bonds markedly lowers the melting point, the bent chains packing less well. Trans-acids have melting points much closer to those of the corresponding saturates. Polymorphism results in two or more solid phases with different melting points. Methyl esters are lower melting than fatty acids but follow similar trends. Fatty acid salts and many polar derivatives of fatty acids are amphiphilic, possessing both hydrophobic and hydrophilic areas within the one molecule. These are surface-active compounds that form monolayer at water/air and water/surface interfaces and micelles in solution. Their surface-active properties are highly dependent on the nature of the polar head group and, to a lesser extent, on the length of the alkyl chain. Most oleo-chemical processes are modifications of the carboxyl group to produce specific surfactants.

Dispersing fatty acids in aqueous solutions is an interesting challenge in the search for environmentally safer surfactants from renewable sources [70, 71]. Moreover, fatty acids are also found in living systems where they are free to participate in the biosynthesis pathway of phospholipids and of the fat-reserve of cells. However, long chain fatty acids form crystals in aqueous solution, and this feature often hampers their use in biochemical and physico chemical studies. However, in particular conditions requiring formation at the water/membrane interface of hydrogen-bond network [72, 73] membrane dispersions can be obtained. This has been emphasized in mixtures of fatty acids and co-surfactants bearing H-group donors [73–77].

Sodium salts of fatty acids are poorly soluble in the case of long alkyl chains, and membranes have been obtained upon varying the pH in the case of potassium salts [78, 79]. However, it was reported that tetra butyl ammonium salts of long chain fatty acids can form both gel phase and micelles [80, 81]. Surprisingly, this type of work is very recent as compared to studies of other alkyl surfactant salts. For instance, the phase behavior of ammonium salts of alkyl sulfate has been more widely reported [82–84]. It seems that there is an open door to the study of the phase behavior of fatty acid salts that was neglected in the past. Dispersing fatty acids in aqueous solutions is also a spring board for further application. Producing foams and emulsions requires that the surfactant used be homogeneously dispersed in water, otherwise, it cannot freely move to the air/water or oil/water interface. Moreover, the depletion of fossil resources and the need for environmentally friendly molecules make fatty acids good candidates for alternative renewable resources, for instance, as surfactants. Sodium dodecyl benzene sulfonate is an anionic surfactant which is used in chemical, biochemical, and industrial works. The effect of SDS on the self-association processes of alcohol and the properties of the solution has been investigated for several systems using a variety of techniques [85–87]. Partial molar volumes and partial molar compressibilities of aqueous solutions of sodium dodecyl sulfate (SDS) and 1-hexanol at pressure up to 140 MPa have been determined [88]. The solution properties of this surfactant have not been examined critically although several papers are available in the literature [89–93]. Viscosities of polymers in solution are associated with cyclic voltammetry [94], interfacial tension [95] which are meticulous by various surfactants have also been investigated. The experimental measurement of the dynamics of surfactants on surfaces and interfaces is extremely challenging, and this is currently possible only for simple geometries [96–102].

Nowadays, hydrocarbon based materials, such as, fatty acid, vegetable oil have prodigious attention to the scientists due to its snow balling demand in many fields, like, biofuels due to environmental concerns, enzyme catalyzed reactions, food and beverage, etc. As a consequence, the necessity of reliable data for a variety of fatty compounds over a large range of process conditions is required. This fact encouraged us to measure viscosity with accuracy adequate for engineering applications. The purpose of the present study is to determine the apparent molar volumes, the apparent molar expansivities and the viscosities of lauric, palmitic and stearic acids in propanol and in SDS soluble propanol in order to understand the solution behavior of these compounds, which are of industrial and biochemical importance.

2.2 Aim of the research

It is important to know the interactions of fatty acids with water in order to examine their function in biological media. However, limited solubilities of long chain fatty acids due to their hydrophobicity restrict the study of the aqueous solution behavior of these compounds. On the other hand, the investigation of solution behaviors of fatty acids in non-aqueous solvents may help us to understand their interaction with water. The study of fatty acid-solvent interactions may also lead us to understand the interactions of solvents with fats, which are triglycerides of fatty acids. Apparent molar volumes and expansivities at infinite dilution and viscosities are important tools to study solute-solvent interactions and have been utilized successfully in various works.

Experimental facts on numerous macroscopic properties (thermodynamic properties, viscosities, surface tension etc.) provide expedient information for appropriate understanding of specific interaction between the components and structure of the solution. The experimental tactic of measurements of several macroscopic properties is also beneficial in providing guidance to theoretical approaches, since the experimentally determined values of solution properties may bring to light certain inadequacies in the anticipated model on which theoretical treatments may be based. The characteristic intermolecular interactions, it is natural to seek functional relationships among the volumetric properties, viscometric properties and thermodynamic properties.

For accurate design of equipment required necessary information regarding the interactions among the components. Equally, knowledge of the viscosity of liquids/mixtures is crucial, 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. Bearing in mind all the above mentioned themes the aim of the present thesis are:

(i) to study the properties of the mixtures/solutions in terms apparent molar volume and viscosity

(ii) to acquire the available data on physico-chemical properties and thermodynamic function of the systems under study

(iii) to comprehend the feasible interaction among the fatty acid+propanol, fatty acid+propanol+SDS and considered systems and

(iv) to understand the effect of SDS on the studied systems.

CHAPTER III

Experimental

3.1 General

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

3.2 Apparatus

The glass-ware used for the measurement for density of solvents and solutions were of the specific gravity bottle (pycnometer). Viscosities of various liquids were measured using the calibrated Ostwald type viscometer. HR 200 electronic balance with an accuracy of ± 0.0001g was used for weighing. 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 (ET-150, Fisher Scientific) with an accuracy of ± 0.05°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 doubled-distilled water at the studied temperature. Calibrated volumetric flask, pipette and burette were used for necessary volume measurement.

3.3 Preparation and Purification of Reagents

High quality analytical grade reagents were used in all the experiments without purification.

3.3.1 Distillation of water

First time water was distilled by water distillation apparatus. First time distilled Water was further purified by a quick-fit glass made distillation apparatus. About 1.5 L water was taken in a round bottom reservoir of which the capacity was 2.0 L. 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 water was used.

3.3.2 Chemicals

Lauric acid, palmitic acid and stearic acid were obtained from Loba Chemie Pvt. Ltd., India. All these acids were analytical grade and were 99.8% pure. The surfactant, sodium dodecyl sulfate was collected from E-Merck, Germany and was 99.9% pure. High performance liquid chromatography (HPLC) grade propanol was collected from E-Merck, India. Chemicals and reagents were of analytical grade and were used without further purification.

3.4 Preparation of solution

Calculated amount of fatty acid and/or SDS was taken in volumetric flask by using weighing bottle and balance. Solutions were prepared by mixing appropriate volumes of propanol up to the mark. Special precaution was taken to prevent evaporation and introduction of moisture or foreign matter into the experimental samples.

3.5 Density measurement

The densities of the solutions were determined by weighing a definite volume of the solution in a pycnometer 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.

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

where, ρ = density of the solution, w = weight of bottle with solution, w_e = weight of empty bottle, v_o = 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°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 carefully in the analytical balance. The difference between the two weights (weight with solution and without solution) gave the weight of the solution in the density bottle. The density measurement was performed for each of the solutions at the temperature 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K respectively in this way using equation (3.1).

3.6 Apparent Molar Volumes measurement:

Apparent molar volumes were determined from measured densities of solvent and solution by using the following equation 1.2.29

$$\varphi_v = \left[\frac{1000(\rho_0 - \rho)}{C\rho_0}\right] + \frac{M_2}{\rho_0} \quad \ldots \quad (1.2.29)$$

where, φ_v is the apparent molar volume, C is the molarity, M_2 is the molecular mass of the solute (fatty acid), and ρ_0 and ρ are the densities of the solvent (propanol) and the solution respectively. In general, φ_v was found to vary linearly with concentration for the systems studied. Thus, φ_v data were fitted into equation1.2.14 and 1.2.19.

$$\varphi_v = \varphi_v^0 + S_v\sqrt{c} \cdots\cdots\cdots\cdots \quad (1.2.14)$$

$$\varphi_v = \varphi_v^0 + S_v\sqrt{C} + b_v C \cdots\cdots\cdots\cdots \quad (1.2.19)$$

where, φ_v is the apparent molar volume at infinite dilution and b_v is an experimentally determined parameter.

3.7 Viscosity measurement

Viscosity of water, fatty acid+propanol and fatty acid+propanol+SDS solutions were measured by using the 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 85°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. 10.0 mL of doubled-distilled water was poured into the viscometer by a pipette.

Then it was allowed to keep in the thermostatic bath for about 30 minutes to attain the bath temperature. With the help of pipette filler attached to the narrower limb of the viscometer, the water was sucked up above the upper mark of the bulb. The water of bulb was then allowed to fall into the capillary and the time of fall between the two marks was noted with the help of stop-watch capable of reading up to 0.01 second. The reading at each temperature was repeated three or four times or even more, 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,

$$\eta = A\rho t \cdots\cdots\cdots\cdots \quad (1.2.25)$$

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

Like water the flow time of different solutions were determined.

3.8 Determination of Thermodynamic Parameters

The values of change of free energy of activation (ΔG*) can be calculated by using the Nightingle and Benck equation [30],

$$\Delta G^* = RTln\left(\frac{\eta V_m}{Nh}\right)\text{..........}(1.2.27)$$

The experimental term in equation 1.2.27 depends on the temperature and is typical for the processes which require activation energy. The activation process to which ΔG* refers cannot be precisely described but in general terms, it corresponds to passes of the system into some relatively favorable configuration, from which it can then easily go to the final state of the molecular process.

Values for the corresponding thermodynamic parameters, enthalpy of activation, ΔH^* and entropy of activation ΔS^* for per mol for viscous flow of the liquids or solutions have been calculated from the relationship (1.2.28).

$$ln\frac{\eta V}{hN} = \frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R} \dots\dots (1.2.28)$$

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

CHAPTER IV

Results and Discussion

4.1 General

The interaction of long chain fatty acids in alcoholic and in surfactant mixed alcoholic medium were investigated. The experimental outcomes and the properties were derived from experimental data are presented in this section. The effort of this chapter include: i) study of interaction between propanol and long chain fatty acids (lauric, palmitic and stearic acid) ii) study of interaction among long chain fatty acids, propanol and SDS iii) determination of volumetric and viscometric properties of the investigated system iv) determination of various thermodynamic parameters such as, free energy, enthalpy, entropy of the experimented systems. From these studies various information were obtained, which are presented in various sections and was discussed in the light of theories stated earlier.

4.2 Volumetric Properties

4.2.1 Density

The densities, ρ of three fatty acids i.e., lauric, palmitic and stearic acids in propanol at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15 K over a concentration range of 0.01–0.4 mol.L^{-1} were investigated. The densities of the propanol done by Assael M. J. *et.al,* are compared with the investigated as shown in table 4.1 for calculations [103]. The densities at varying molarities (0.01–0.4M) of the stated fatty acid (lauric, palmitic and stearic acid) solutions in propanol have been shown in table 4.2 at different temperatures. Comparing the results in table 4.1 and table 4.2 it can be stated that densities of all the solutions of fatty acids in propanol are higher than those of the pure propanol. Densities of lauric, palmitic, and stearic acids in propanol increased remarkably with concentrations at all the temperatures. Results of table 4.2 are fitted in figures 4.1–4.3. From the figure 4.1 it is seen that densities of lauric acid in propanol increased almost linearly with the concentration of the acid within the temperatures range of 298.15 K to 318.15 K at 5 K intervals. Similar results were obtained for palmitic and stearic acids. The increase of densities of all acids with concentrations can be attributed to the increase in both solute–solvent and solute–solute interactions. At the same time it is seen that the density values decrease significantly with increasing temperature at a constant concentration (as shown in table 4.2). With the increase of temperature the internal energies of the systems are increased and the solute-solvent and solute-solute interactions might be weakened. The consequence is the decrease in densities. It is also seen that densities of fatty acids in propanol increased with carbon number of the fatty acids at all concentrations at a constant temperature as shown in table 4.2 and figure 4.4–4.9 although there are deviations in few cases which can be accomplished as experimental error. The increase in densities with carbon number can be explained by the increase in both molecular mass of the fatty acids and the degree of solute-solvent interactions with carbon number. The sharp change in density values with carbon number of fatty acids may make a significant contribution to apparent molar volumes, viscosities and other properties in solution. The density data also showed a good agreement with [104] the similar unpublished results in propanol solution done in the same laboratory [105] although the values in butanol and propanol system are relatively higher. This may be greater interaction of relatively longer $CH_3CH_2CH_2CH_2$- group of butanol and $CH_3CH_2CH_2$- group of propanol than CH_3CH_2- of ethanol with the hydrophobic part of long chain fatty acids. Moreover, a close inspection of the density data from various tables suggests densities versus concentration, which might give a considerable increase in apparent molar volumes, has been discussed later.

Table- 4.1: Theoretical [111] and experimental value of density and viscosity of propanol

Temperature	Density		Viscosity	
	Theoretical	Experimental	Theoretical	Experimental
298.15K	0.7993	0.803748	1.954	1.9301
303.15K	0.7953	0.802540	1.734	1.7176
308.15K	0.7913	0.798940	1.545	1.5231
313.15K	0.7873	0.794916	1.384	1.3485
318.15K	0.7832	0.791104	1.241	1.2069
323.15K	0.7790	0.787180	1.116	1.0845

Table-4.2: Densities (g cm^{-3}) of lauric, palmitic and stearic acid in propanol system at 298.15K, 303.5 K, 308.5 K, 313.15 K, 318.15 K and 323.15 K

Name of the system	Conc./ mol.L^{-1}	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
Lauric Acid+ Propanol	0.0100	0.8049	0.8036	0.7999	0.7957	0.7918	0.7878
	0.0500	0.8065	0.8047	0.8008	0.7965	0.7926	0.7886
	0.1000	0.8075	0.8058	0.8017	0.7971	0.7932	0.7893
	0.2000	0.8100	0.8075	0.8037	0.7992	0.7952	0.7914
	0.3000	0.8120	0.8090	0.8056	0.8012	0.7971	0.7934
	0.4000	0.8141	0.8108	0.8073	0.8033	0.7990	0.7954
Palmitic Acid+ Propanol	0.0100	0.8054	0.8041	0.8004	0.7962	0.7923	0.7881
	0.0500	0.8073	0.8053	0.8014	0.7971	0.7932	0.7893
	0.1000	0.8085	0.8056	0.8027	0.7981	0.7939	0.7903
	0.2000	0.8107	0.8085	0.8043	0.8004	0.7959	0.7921
	0.3000	0.8127	0.8098	0.8062	0.8024	0.7976	0.7939
	0.4000	0.8146	0.8120	0.8083	0.8046	0.7994	0.7958
Stearic Acid+ Propanol	0.0100	0.8055	0.8043	0.8006	0.7964	0.7924	0.7882
	0.0500	0.8077	0.8056	0.8016	0.7976	0.7933	0.7893
	0.1000	0.8087	0.8071	0.8026	0.7986	0.7941	0.7902
	0.2000	0.8114	0.8093	0.8044	0.8002	0.7960	0.7923
	0.3000	0.8132	0.8110	0.8062	0.8025	0.7977	0.7940
	0.4000	0.8146	0.8128	0.8086	0.8047	0.7995	0.7960

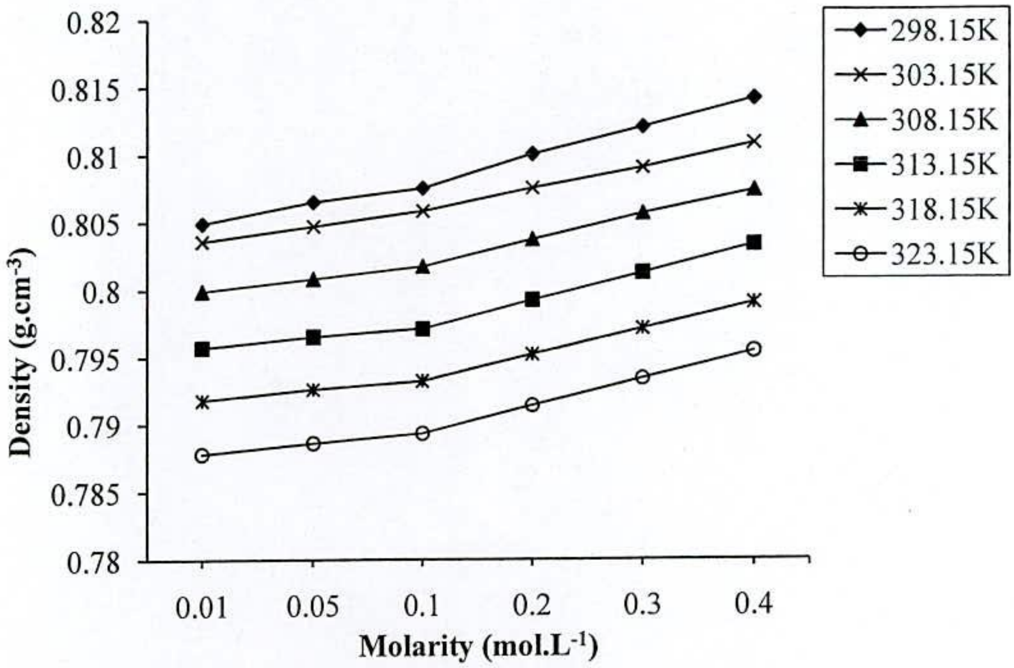


Figure-4.1: **Densities (ρ) of lauric acid in propanol at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K**

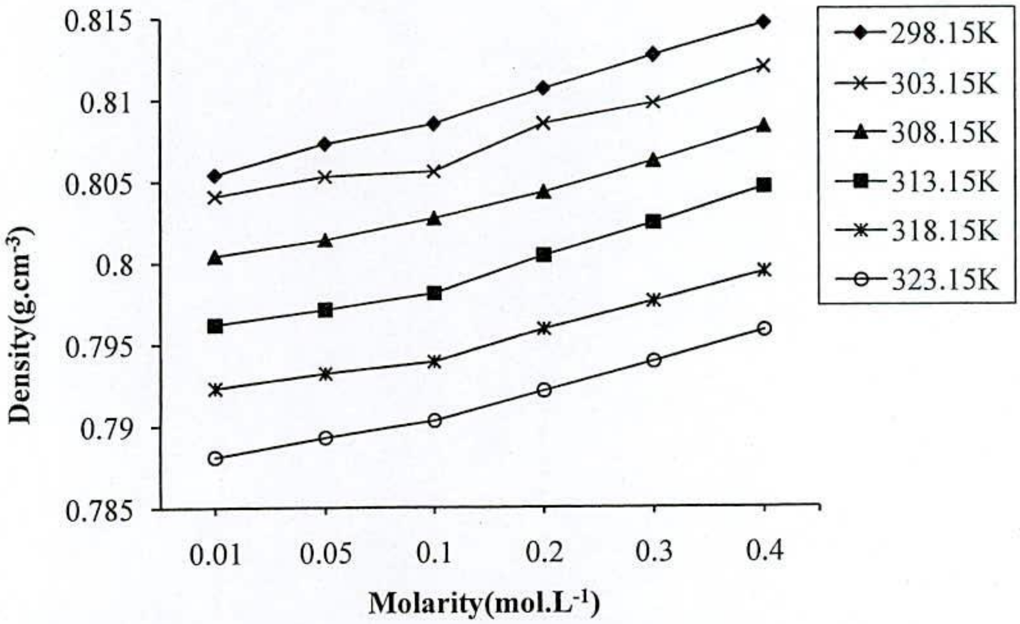


Figure-4.2: Density (ρ) of Palmitic acid in propanol at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K

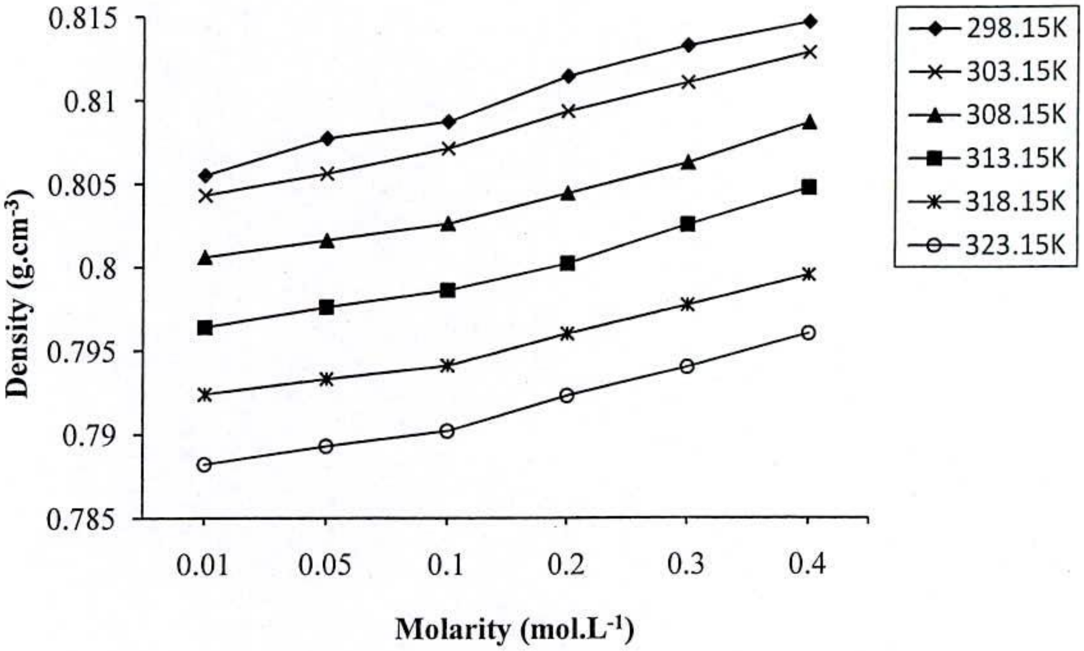


Figure- 4.3: Density (ρ) of Stearic acid in propanol at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K

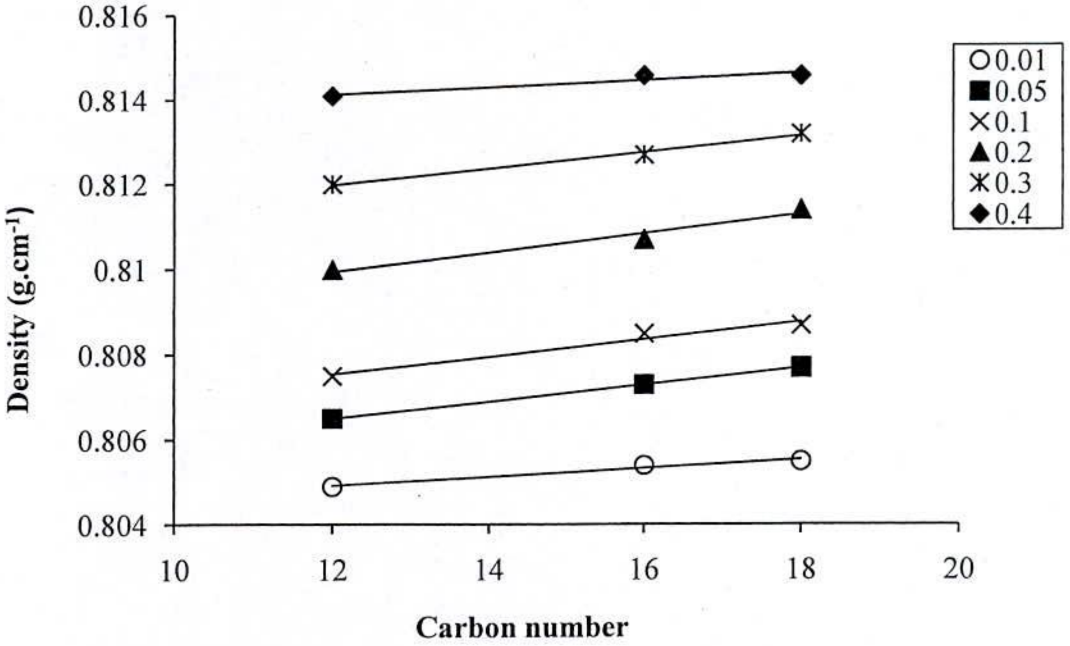


Figure-4.4: Densities of Lauric, Palmitic and Stearic acid at all concentrations at 298.15K

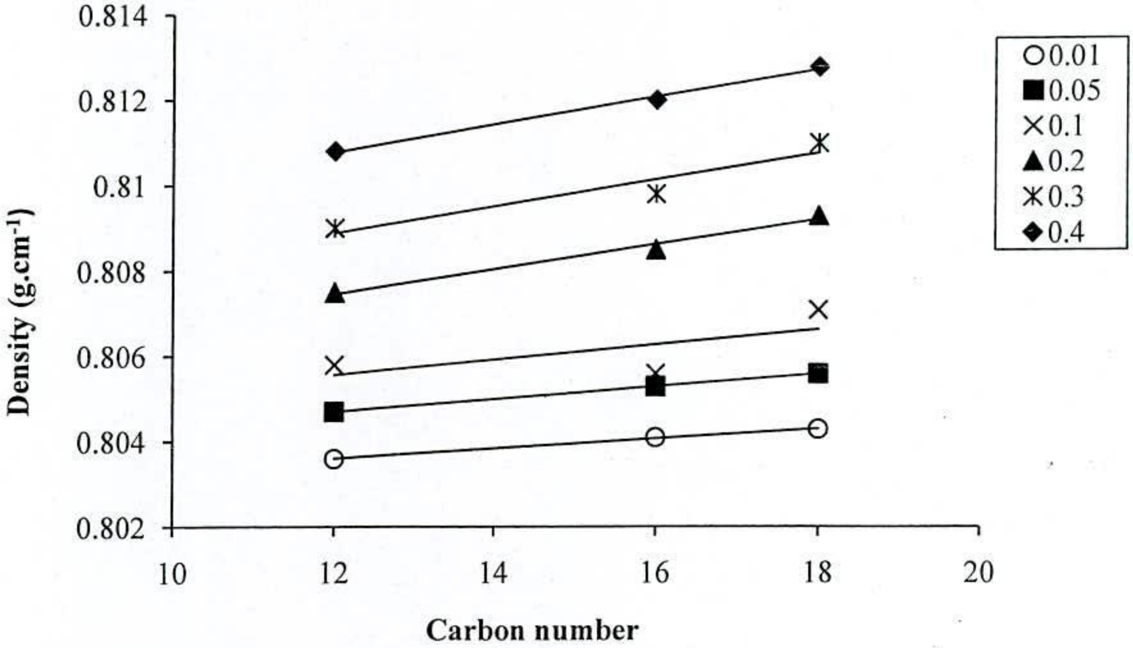


Figure-4.5: Densities of Lauric, Palmitic and Stearic acid at all concentrations at 303.15K

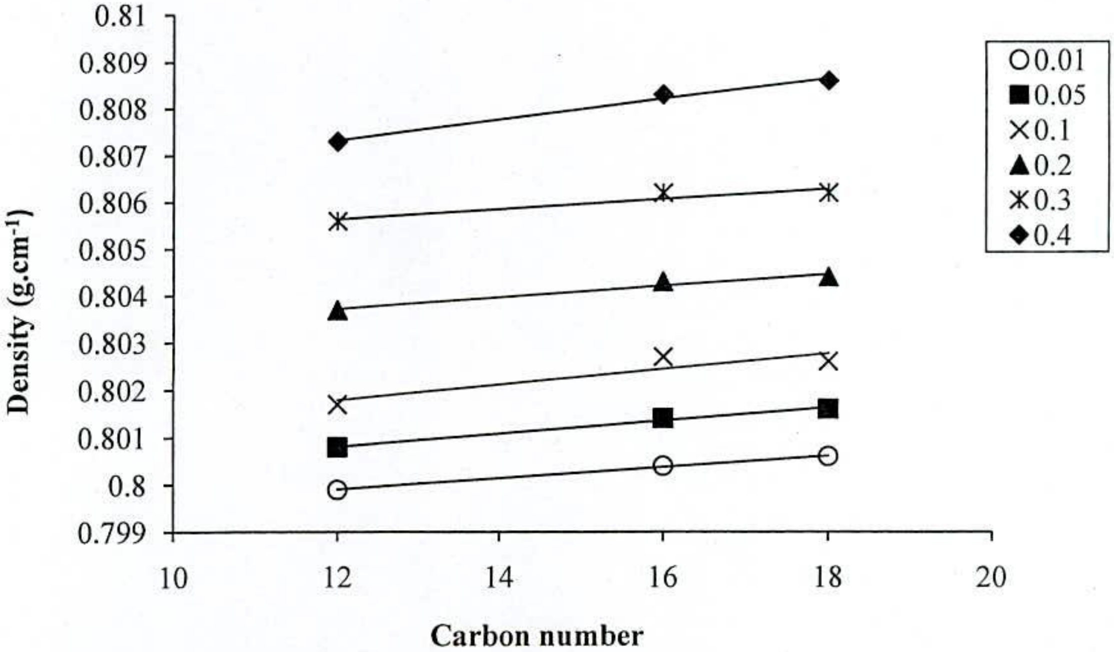


Figure-4.6: Densities of Lauric, Palmitic and Stearic acid at all concentrations at 308.15K

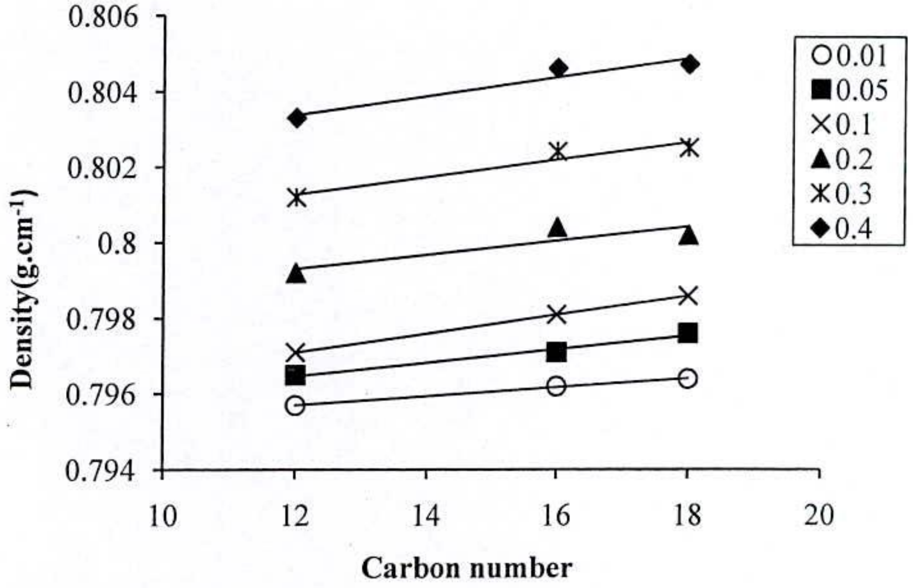


Figure-4.7: Densities of Lauric, Palmitic and Stearic acid at all concentrations at 313.15K

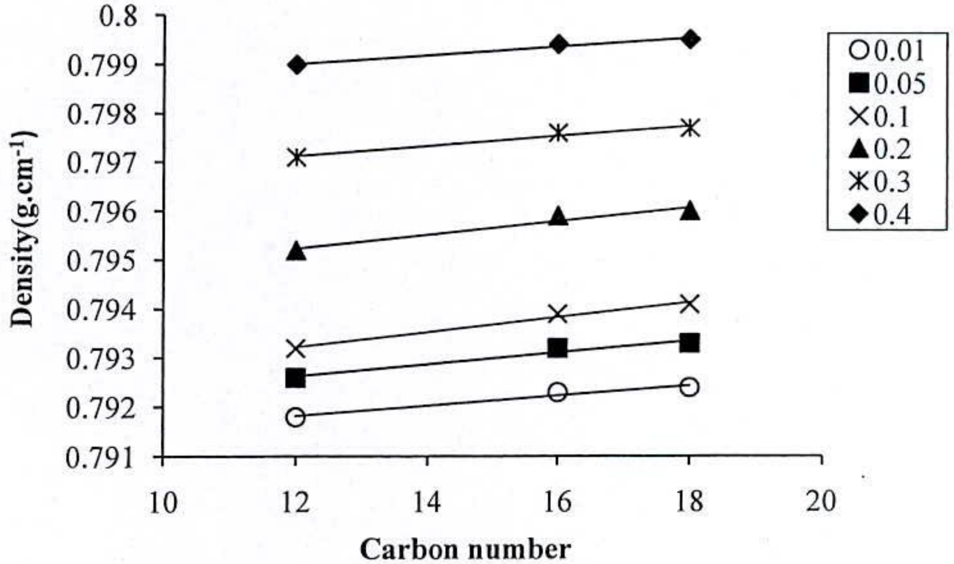


Figure-4.8: Densities of Lauric, Palmitic and Stearic acid at all concentrations at 318.15K

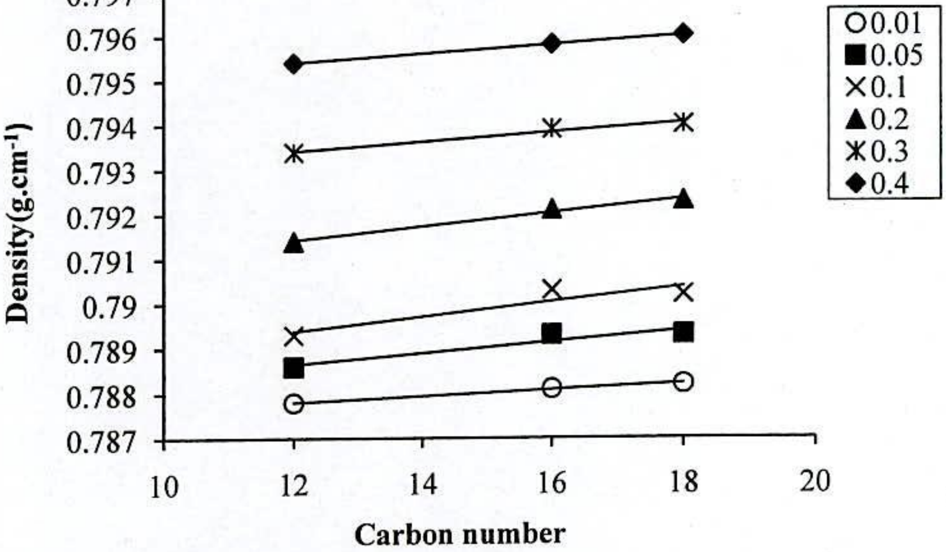


Figure-4.9: Densities of Lauric, Palmitic and Stearic acid at all concentrations at 323.15K

The effect of addition of surfactant, SDS to (fatty acid + propanol) systems has also been studied. The investigated concentrations of SDS were 0.001M and 0.005 M. Table 4.3-4.4 and figures 4.10–4.15 showed the plots of corresponding densities as well as the effect of addition of SDS to (fatty acid+ propanol) systems. From the figures, it is seen that the ultimate pattern of density behavior of lauric, palmitic and stearic acids in 0.001M SDS and 0.005M SDS solution is almost similar to those of propanol systems. Figure 4.10 it is seen that densities of lauric acid + propanol in presence of 0.001M SDS system increased almost linearly with the concentration of the acid within the temperatures range of 298.15 K to 318.15 K at 5 K intervals. Similar results were obtained for palmitic and stearic acids and are shown in figure 4.11 and 4.12. Fatty acids in propanol and 0.005M SDS system showed the almost similar trend as shown in figure 4.13-4.15. The densities increased positively at both concentrations of SDS in comparison to corresponding systems without SDS than those of pure propanol-1. These results confer that at molecular arrangements in SDS to (fatty acid + propanol) systems more organized than corresponding systems without SDS. These results can be explained in terms of the establishment of additional hydrophobic interactions among the hydrophobic parts of the surfactant, fatty acids and propanol. It is also seen that the density values of 0.005M SDS in (fatty acid+ propanol) systems are higher than those of 0.001M SDS in the corresponding solutions which indicates hydrophobic interactions among the hydrophobic parts of the surfactant increases with the concentration of surfactant, SDS. Solution become viscous with addition of excess SDS than 0.005M and normal viscometer doesn't work to carry out the experiment.

The values of densities in SDS systems were found to in the order of:

Alcohol–Fatty acid–0.005 M SDS> Alcohol–Fatty acid–0.001 M SDS>Alcohol–Fatty acid

Table-4.3: Densities (g.cm $^{-3}$) of lauric ,palmitic and stearic acid in propanol in presence of 0.001 M SDS system at 298.15 K, 303.15 K, 308.15 K, 313.15 K, 318.15 K and 323.15 K

Name of the system	Conc./ mol.L^{-1}	298.15K	303.15 K	308.15K	313.15 K	318.15 K	323.15K
Lauric Acid +Propanol+ 0.001M SDS	0.0100	0.8051	0.8037	0.8000	0.7959	0.7921	0.7879
	0.0500	0.8069	0.8053	0.8013	0.7973	0.7935	0.7889
	0.1000	0.8081	0.8062	0.8023	0.7982	0.7943	0.7898
	0.2000	0.8103	0.8081	0.8045	0.8004	0.7964	0.7917
	0.3000	0.8127	0.8100	0.8064	0.8024	0.7985	0.7940
	0.4000	0.8146	0.8119	0.8087	0.8048	0.8005	0.7960
Palmitic Acid +Propanol+ 0.001M SDS	0.0100	0.8055	0.8043	0.8007	0.7965	0.7926	0.7886
	0.0500	0.8081	0.8061	0.8021	0.7980	0.7938	0.7899
	0.1000	0.8093	0.8070	0.8031	0.7989	0.7949	0.7906
	0.2000	0.8112	0.8090	0.8047	0.8011	0.7971	0.7924
	0.3000	0.8131	0.8112	0.8064	0.8026	0.7990	0.7947
	0.4000	0.8151	0.8130	0.8087	0.8049	0.8011	0.7967
Stearic Acid +Propanol+ 0.001M SDS	0.0100	0.8056	0.8041	0.8004	0.7963	0.7923	0.7881
	0.0500	0.8083	0.8064	0.8023	0.7976	0.7934	0.7895
	0.1000	0.8095	0.8072	0.8026	0.7985	0.7942	0.7905
	0.2000	0.8121	0.8097	0.8046	0.8003	0.7967	0.7924
	0.3000	0.8143	0.8113	0.8068	0.8026	0.7980	0.7943
	0.4000	0.8161	0.8130	0.8089	0.8049	0.8001	0.7961

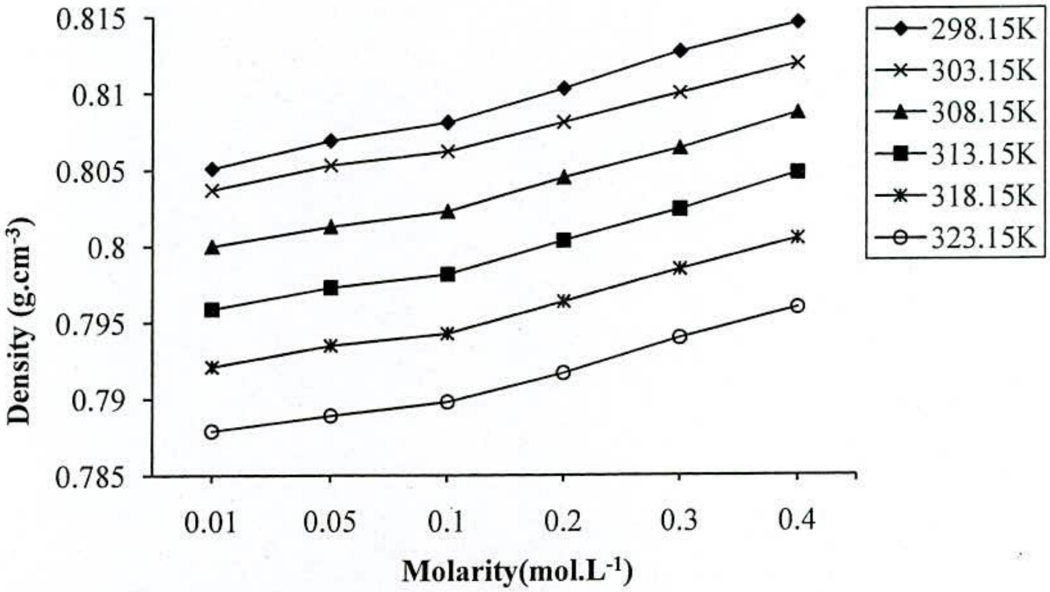


Figure-4.10: Densities (ρ) of lauric acid + propanol in presence of 0.001 M SDS system at 298.15 K, 303.15 K, 308.15 K, 313.15 K, 318.15 K and 323.15K

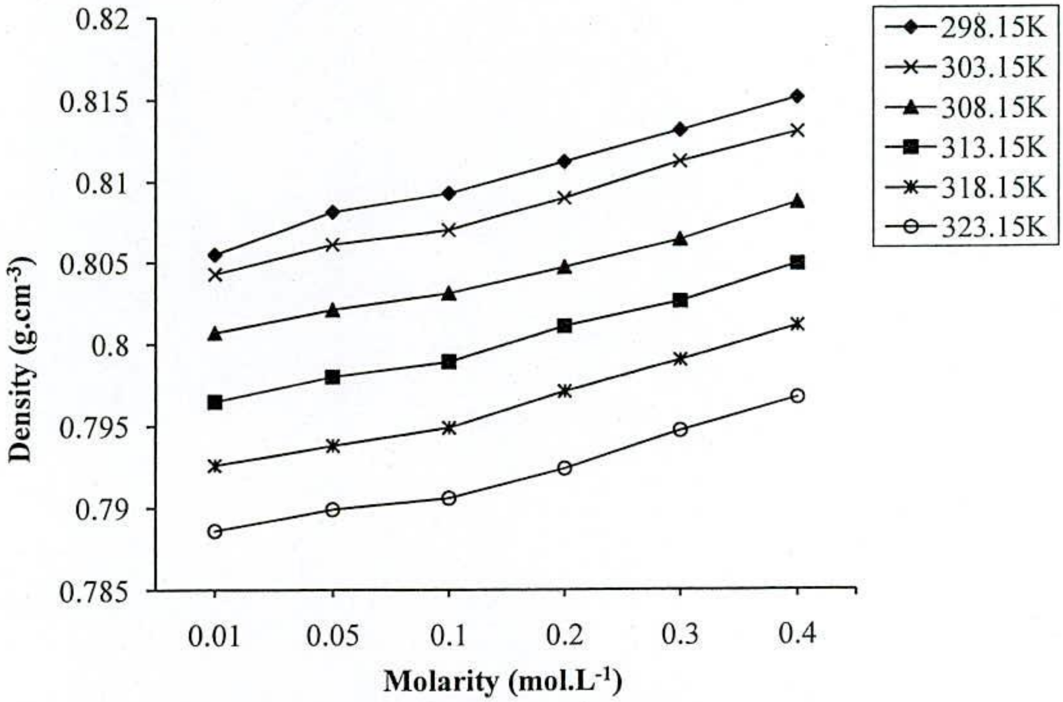


Figure-4.11: Densities (ρ) of palmitic acid + propanol in presence of 0.001 M SDS system at 298.15 K, 303.15 K, 308.15 K, 313.15 K, 318.15 K and 323.15K

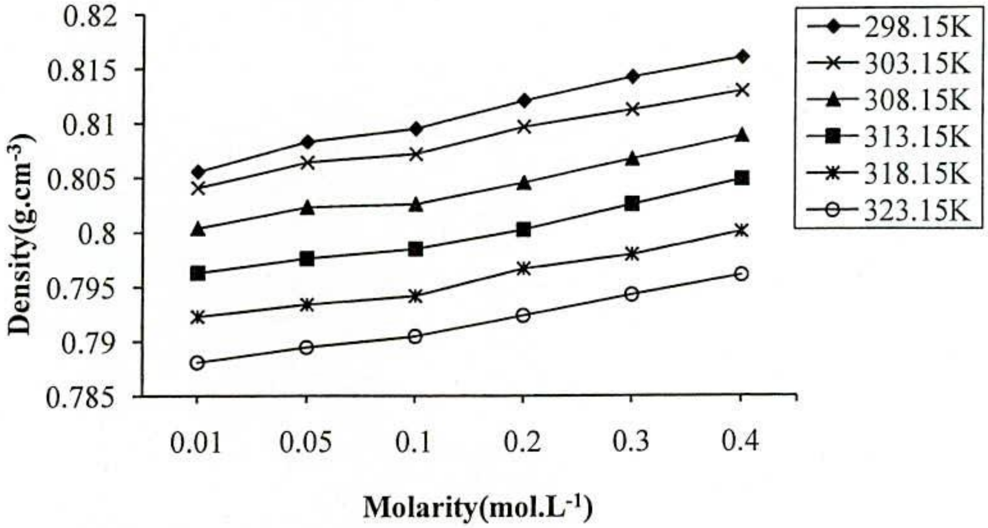


Figure-4.12: Densities (ρ) of stearic acid + propanol in presence of 0.001 M SDS system at 298.15 K, 303.15 K, 308.15 K, 313.15 K, 318.15 K and 323.15K

Table-4.4: Densities (g.cm $^{-3}$) of lauric, palmitic and stearic acid in propanol in presence of 0.005 M SDS system at 298.15 K, 303.15 K, 308.15 K, 313.1K, 318.15 K and 323.15 K

Name of the system	Conc./ mol.L^{-1}	298.15K	303.15 K	308.15K	313.15 K	318.15 K	323.15K
Lauric Acid +Propanol+ 0.005M SDS	0.0100	0.8053	0.8039	0.8002	0.7961	0.7922	0.7880
	0.0500	0.8077	0.8060	0.8019	0.7986	0.7936	0.7890
	0.1000	0.8091	0.8069	0.8027	0.7999	0.7948	0.7900
	0.2000	0.8106	0.8084	0.8055	0.8014	0.7968	0.7918
	0.3000	0.8134	0.8104	0.8065	0.8030	0.7993	0.7941
	0.4000	0.8151	0.8124	0.8090	0.8049	0.8006	0.7964
Palmitic Acid +Propanol+ 0.005M SDS	0.0100	0.8057	0.8043	0.8005	0.7967	0.7925	0.7885
	0.0500	0.8087	0.8062	0.8026	0.7985	0.7940	0.7901
	0.1000	0.8101	0.8072	0.8035	0.7990	0.7957	0.7907
	0.2000	0.8117	0.8092	0.8052	0.8013	0.7974	0.7926
	0.3000	0.8135	0.8114	0.8076	0.8028	0.8011	0.7950
	0.4000	0.8156	0.8134	0.8089	0.8052	0.8019	0.7970
Stearic Acid +Propanol+ 0.005M SDS	0.0100	0.8058	0.8043	0.8006	0.7965	0.7925	0.7883
	0.0500	0.8095	0.8066	0.8026	0.7992	0.7946	0.7901
	0.1000	0.8110	0.8079	0.8036	0.8002	0.7957	0.7910
	0.2000	0.8132	0.8099	0.8059	0.8030	0.7985	0.7927
	0.3000	0.8154	0.8115	0.8084	0.8057	0.7991	0.7948
	0.4000	0.8176	0.8132	0.8099	0.8068	0.8033	0.7977

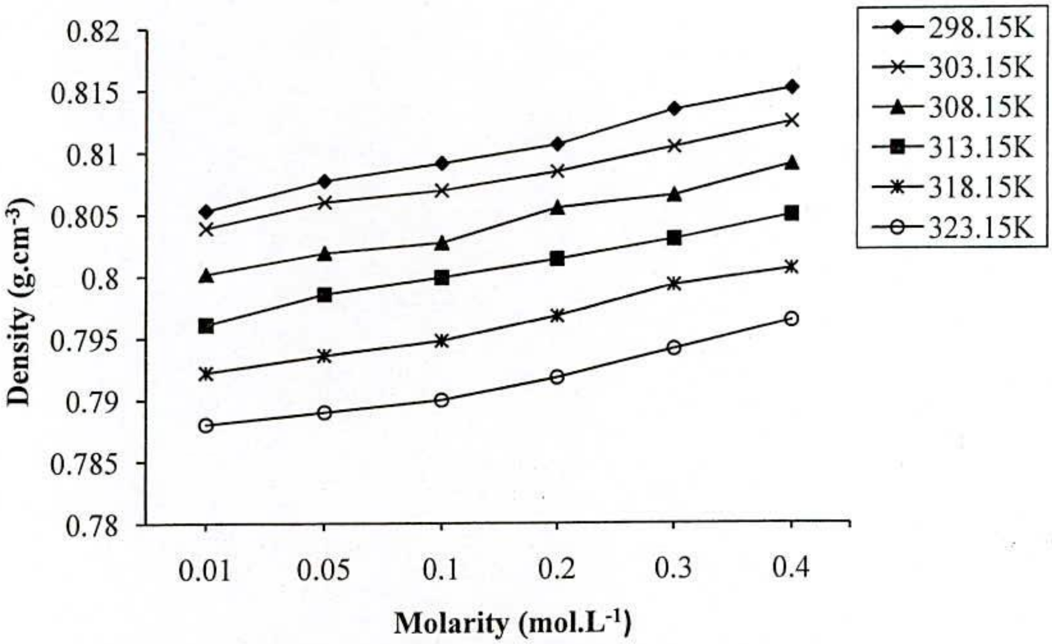


Figure-4.13: Densities (ρ) of lauric acid + propanol in presence of 0.005 M SDS system at 298.15 K, 303.15 K, 308.15 K,313.15 K,318.15 K and 323.15 K

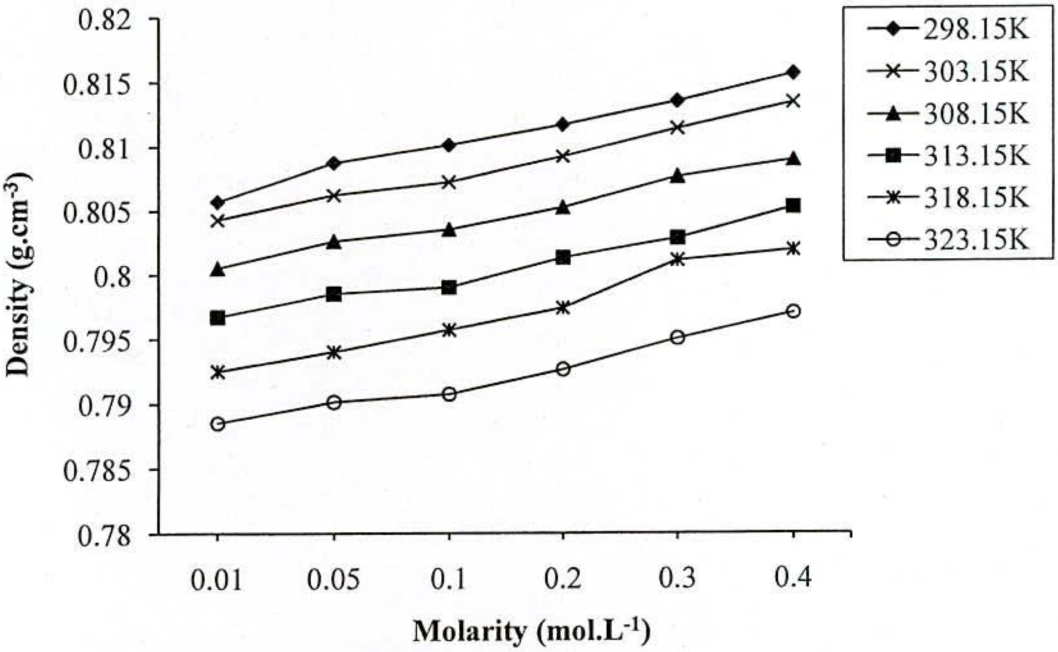


Figure-4.14: Densities (ρ) of palmitic acid + propanol in presence of 0.005 M SDS system at 298.15 K, 303.15 K, 308.15 K, 313.15 K,318.15 K and 323.15 K

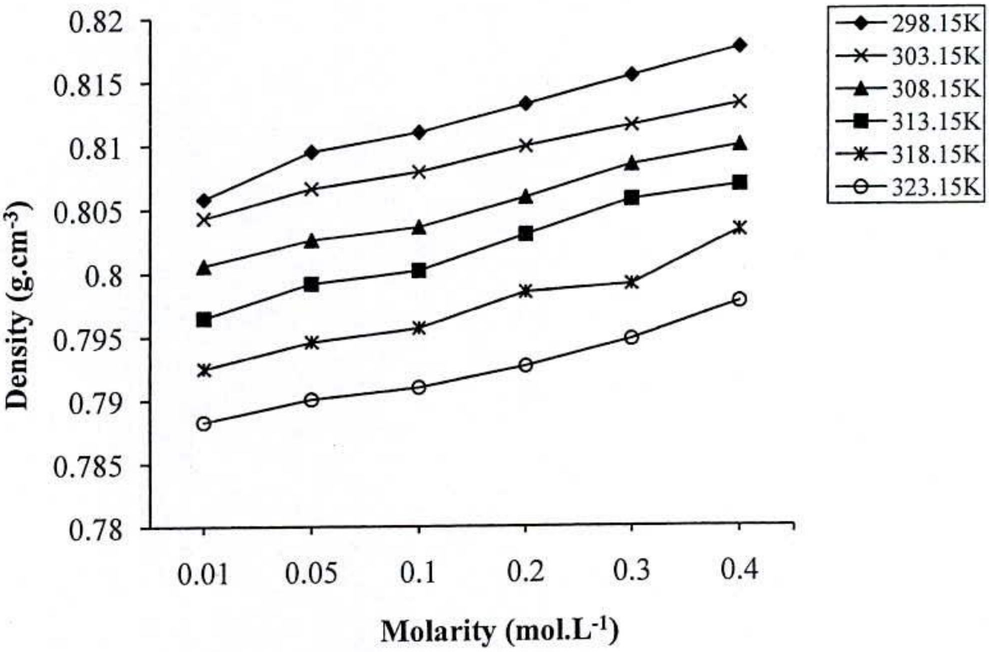


Figure-4.15: Densities(ρ) of stearic acid + propanol in presence of 0.005 M SDS system at 298.15 K, 303.15 K, 308.15 K, 313.15 K,318.15 K and 323.15 K

4.2.2 Apparent molar volumes

The apparent molar volumes, of lauric, palmitic and stearic acids in propanol have been determined at different concentrations and at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15 K temperatures using equation 1.2.9. The values of of at different temperatures have been shown in table 4.5. It is seen that apparent molar volume is dependent upon the concentration of fatty acids as well as on the temperature. The values have been found to be positive throughout the whole concentration range for all acids in propanol. The apparent molar volumes, of all fatty acids in propanol were found to be increased with concentration at all temperatures. Similarly, values were found to be increased with increasing temperature at any concentration of the solution. These results may be due to the solute–solvent and solute–solute interaction in the solutions. It may also be assumed as the concentration increases because solute–solute interactions start to gain importance in addition to solute-solvent interactions. This shows that $\varphi_v$values are strongly dependent upon concentration as well as the temperature. The $\varphi_v$values are also found to be increased with the chain length of the fatty acids and this may be due to the hydrophobic characters of alkyl chain towards CH_3CH_2- group of propanol. It can be conferred that the number of carbon atoms in the hydrocarbon chain of the fatty acid is proportional to the degree of hydrophobic/hydrophilic balance of the whole compound [106]. It is clearly seen that stearic acid has the highest φ_v values at all temperatures than palmitic and the lowest one is lauric acid. Figures 4.16–4.18 show the plots of apparent molar volumes, φ_v versus square root of concentration of different fatty acids in propanol at different temperatures. From the figures it is seen that φ_v values increased square root of concentrations and temperatures exponentially. At the same time the level of increase of apparent molar volumes is relatively substantial at higher temperatures. After 0.2 M the increase of apparent molar volumes was plodding can be governed primarily by the entropy increase experiencing the more hydrophobic environment. Figures 4.16–4.18 also show the plots of apparent molar volumes, φ_v versus square root of concentration of different fatty acids in propanol at a definite temperature with very little exceptions which may be due to the experimental error.

The apparent molar volumes, φ_v of fatty acids at all concentrations and temperatures in propanol have been found to be in the order of:

Stearic acid – propanol > Palmitic acid – propanol > Lauric acid – propanol

From the above discussion about apparent molar volume reveals the following characteristics:

i) The addition of fatty acids in alcohol is accompanied by considerable expansion of apparent molar volume, $\boldsymbol{\varphi_v}$ are positive and large in magnitude.

ii) Temperature effect on $\boldsymbol{\varphi_v}$ is quite significant.

iii) Concentration effect on $\boldsymbol{\varphi_v}$ is also significant, but it should be mentioned that concentration beyond 0.35 M could not be investigated because of the limited solubility of the fatty acids in propanol.

iv) With increasing chain length the $\boldsymbol{\varphi}_{\boldsymbol{v}}$values have been increased.

The pattern of apparent molar volumes of lauric, palmitic and stearic acids in 0.001 M and 0.005 M SDS solution is very similar to those of (propanol + fatty acid) systems as shown in table 4.6–4.7 and figure 4.19–4.24. The apparent molar volumes increased at all concentration of SDS in comparison to corresponding systems without SDS. The increase of apparent molar volumes of different fatty acids in propanol in presence of surfactant sustains those of density values as discussed earlier. These results can be explained in terms of the establishment of additional hydrophobic interactions among the hydrophobic parts of the surfactant, fatty acids and propanol. It is also seen that the density values of 0.005M SDS in (fatty acid+ propanol) systems are higher than those of 0.001M SDS in the corresponding solutions which indicates hydrophobic interactions among the hydrophobic parts of the surfactant increases with the concentration of surfactant, SDS. The results conferred that at molecular arrangements in SDS to (fatty acid + propanol) systems more organized than corresponding systems without SDS.

Table-4.5: Apparent Molar Volume (cm^3.mol^{-1}) of lauric, palmitic and stearic acid in propanol system at 298.15 K, 303.15 K, 308.15 K, 313.15 K, 318.15 K and 323.15 K

Name of the system	Conc./ mol.L^{-1}	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
Lauric Acid+ Propanol	0.0100	105.90	117.53	130.57	153.37	165.24	175.72
	0.0500	180.75	195.78	204.17	212.15	215.40	218.40
	0.1000	202.55	208.99	216.19	224.53	226.72	227.55
	0.2000	210.34	218.71	220.94	225.06	227.33	227.67
	0.3000	215.01	222.78	222.95	225.65	227.95	228.14
	0.4000	217.03	223.88	224.57	225.63	228.26	228.37
Palmitic Acid+ Propanol	0.0100	113.51	125.14	138.22	161.06	172.96	208.88
	0.0500	230.66	250.74	259.38	267.64	271.15	271.89
	0.1000	259.92	281.39	273.90	282.53	288.80	286.12
	0.2000	275.80	282.39	287.42	288.09	293.83	294.51
	0.3000	281.92	289.37	290.67	291.20	296.77	297.30
	0.4000	285.29	290.05	291.67	292.13	297.93	298.38
Stearic Acid+ Propanol	0.0100	135.96	135.17	148.30	171.19	195.78	231.81
	0.0500	255.60	278.22	289.48	290.35	304.08	307.53
	0.1000	292.33	297.65	310.26	311.53	321.73	323.03
	0.2000	306.34	312.36	321.90	324.64	328.65	328.87
	0.3000	314.74	319.34	325.78	326.07	331.81	332.51
	0.4000	320.19	322.51	325.84	327.10	333.07	333.38

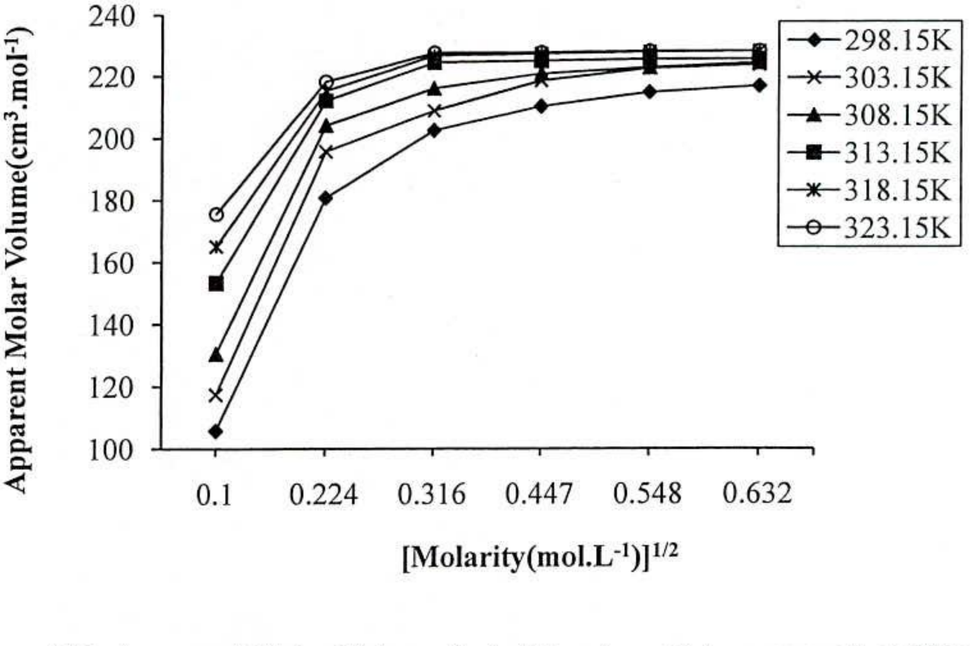


Figure-4.16: Apparent Molar Volume (φ_v) of lauric acid in propanol at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K

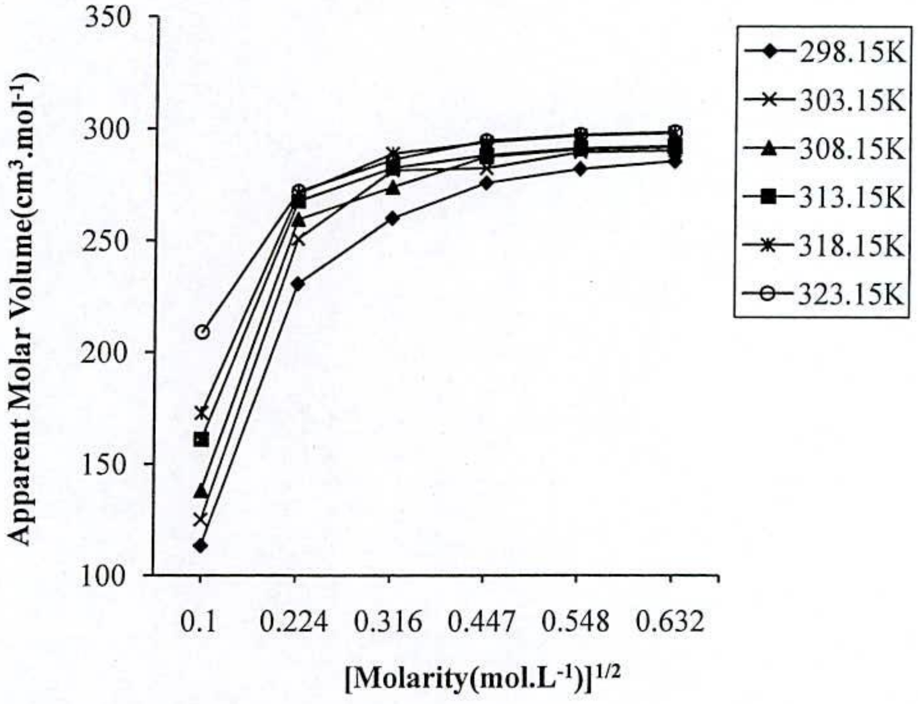


Figure-4.17: Apparent Molar Volume (φ_v) of Palmitic acid in propanol at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K

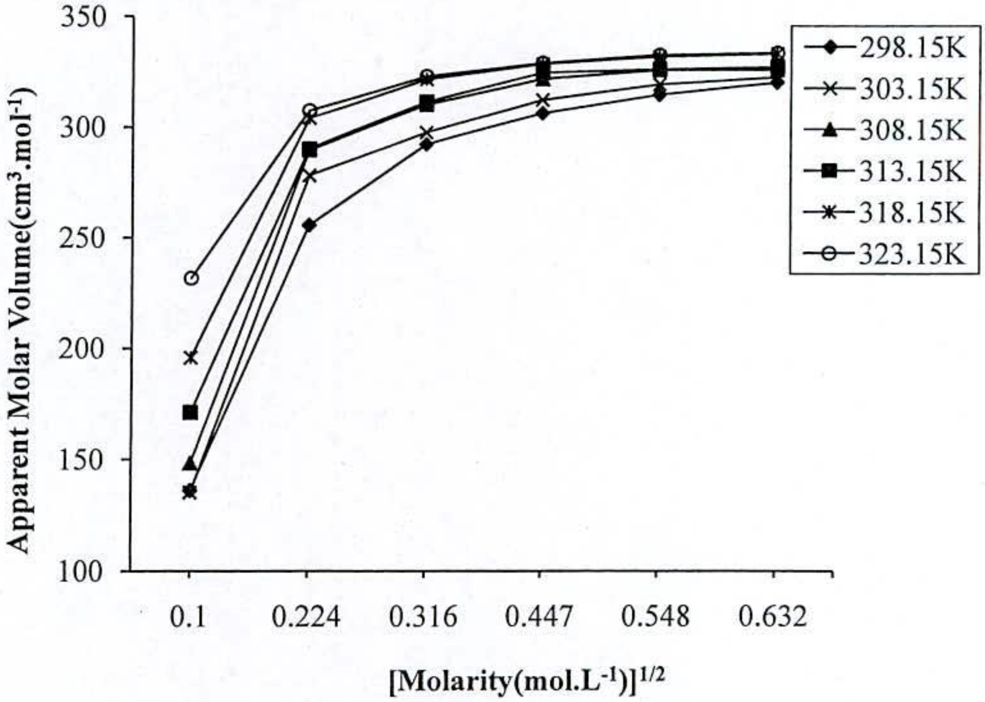


Figure-4.18: Apparent Molar Volume (φ_v) of Stearic acid in propanol at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K

Table-4.6: Apparent Molar Volume ($cm^3.mol^{-1}$) of lauric, palmitic and stearic acid in propanol in presence of 0.001 M SDS system at 298.15K, 303.15K, 308.15 K, 313.15 K, 318.15 K and 323.15 K

Name of the system	Conc./ $mol.L^{-1}$	298.15K	303.15 K	308.15K	313.15 K	318.15 K	323.15K
Lauric Acid +Propanol+ .001M SDS	0.0100	75.80	100.09	113.31	122.56	121.76	157.43
	0.0500	169.76	179.84	190.71	190.90	191.54	209.67
	0.1000	194.57	203.51	208.21	210.13	212.27	220.65
	0.2000	208.22	214.73	215.71	217.24	219.48	225.50
	0.3000	211.94	218.47	219.46	220.44	221.88	225.42
	0.4000	215.36	220.34	220.08	220.79	223.40	226.34
Palmitic Acid +Propanol+ .001M SDS	0.0100	95.84	95.24	95.92	117.67	129.48	139.79
	0.0500	209.72	229.82	240.92	243.88	254.89	255.55
	0.1000	249.46	263.46	268.43	271.92	275.62	281.77
	0.2000	272.44	279.04	284.69	283.42	285.98	292.34
	0.3000	280.10	283.40	289.69	290.19	290.70	293.74
	0.4000	283.62	286.83	290.32	291.06	292.43	295.40
Stearic Acid +Propanol+ .001M SDS	0.0100	118.30	155.12	168.58	178.12	202.87	238.94
	0.0500	239.64	257.30	271.02	289.23	300.46	301.35
	0.1000	281.87	295.93	309.80	312.24	319.93	318.67
	0.2000	301.74	309.63	320.43	323.74	323.97	327.97
	0.3000	310.02	317.94	323.14	325.48	330.38	331.07
	0.4000	315.41	321.78	324.80	326.35	331.05	332.94

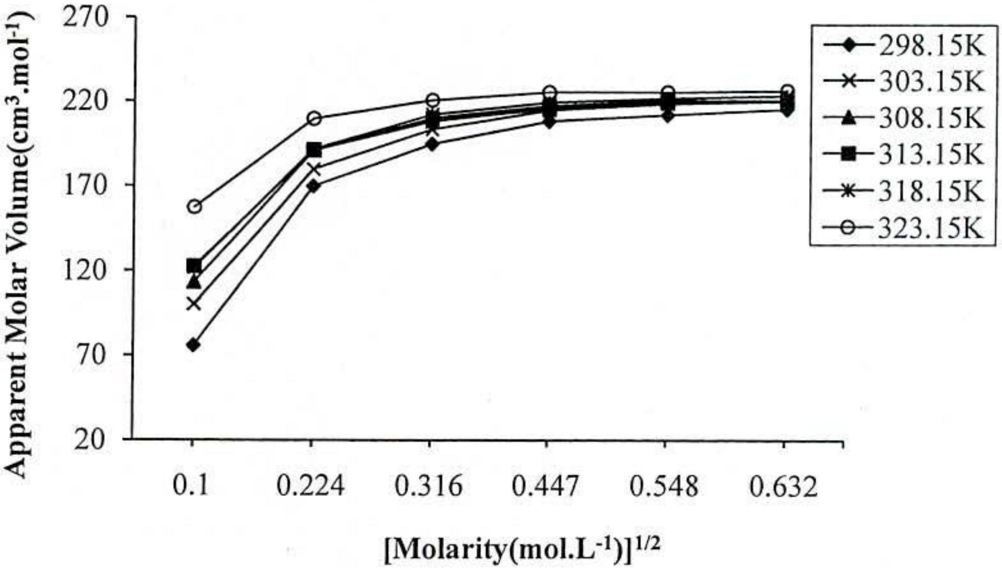


Figure-4.19: Apparent Molar Volume (φ_υ) of lauric acid in propanol in presence of 0.001M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K

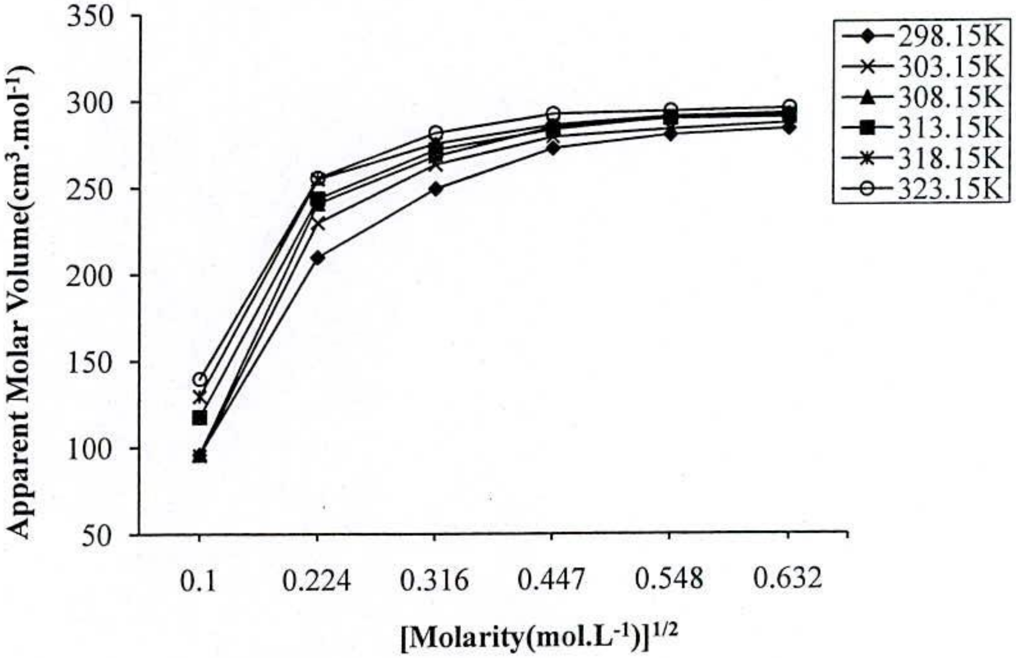


Figure-4.20: Apparent Molar Volume (φ_v) of Palmitic acid in propanol in presence of 0.001 M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K

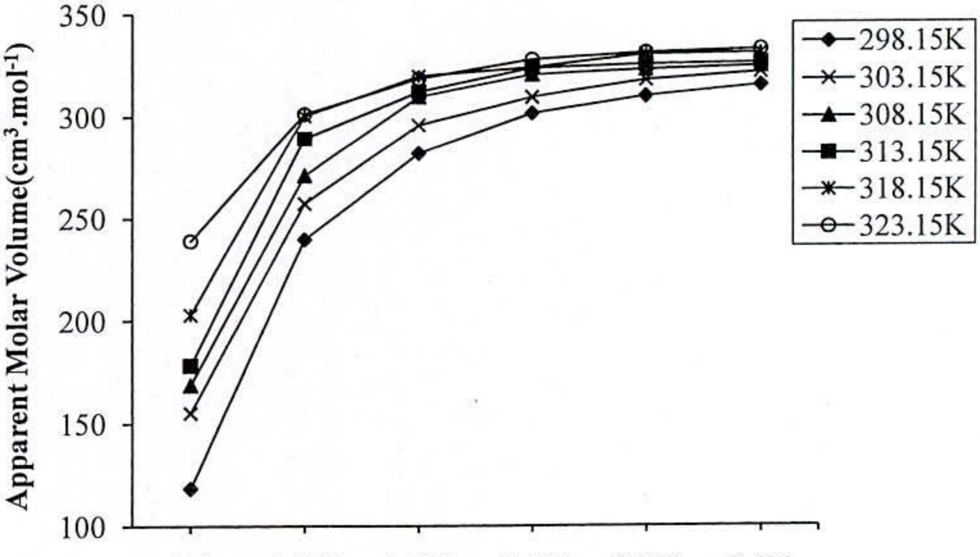


Figure-4.21: Apparent Molar Volume (φ_v) of Stearic acid in propanol in presence of 0.001M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K

Table-4.7: Apparent Molar Volume ($cm^3.mol^{-1}$) of lauric, palmitic and stearic acid in propanol in presence of 0.005 M SDS system at 298.15K, 303.15K, 308.15 K, 313.15 K, 318.15 K and 323.15 K

Name of the system	Conc./ $mol.L^{-1}$	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
Lauric Acid +Propanol+ 0.005M SDS	0.0100	44.57	68.69	81.39	91.24	102.68	137.88
	0.0500	148.60	161.11	174.33	156.97	187.73	205.77
	0.1000	181.51	194.16	202.53	188.14	205.32	217.44
	0.2000	206.05	212.55	209.12	210.65	216.64	224.54
	0.3000	208.84	216.60	218.83	217.73	218.31	224.79
	0.4000	213.66	218.63	218.99	220.33	222.93	224.91
Palmitic Acid +Propanol+ 0.005M SDS	0.0100	64.62	88.77	114.08	86.35	135.69	145.64
	0.0500	193.53	226.05	227.04	230.08	248.56	249.11
	0.1000	238.88	260.34	262.75	270.06	264.88	279.83
	0.2000	269.03	277.49	281.24	281.87	283.78	290.74
	0.3000	278.25	282.37	284.48	289.17	281.66	292.27
	0.4000	281.92	285.44	289.54	289.98	289.76	294.30
Stearic Acid +Propanol+ 0.005M SDS	0.0100	87.08	123.72	136.67	146.80	171.15	206.69
	0.0500	208.52	251.03	262.15	247.75	268.85	284.75
	0.1000	262.59	286.57	296.61	290.25	300.34	311.66
	0.2000	294.60	308.08	311.97	306.47	312.29	325.75
	0.3000	305.27	316.91	316.25	312.30	325.55	328.75
	0.4000	310.60	321.02	321.52	320.24	320.80	327.71

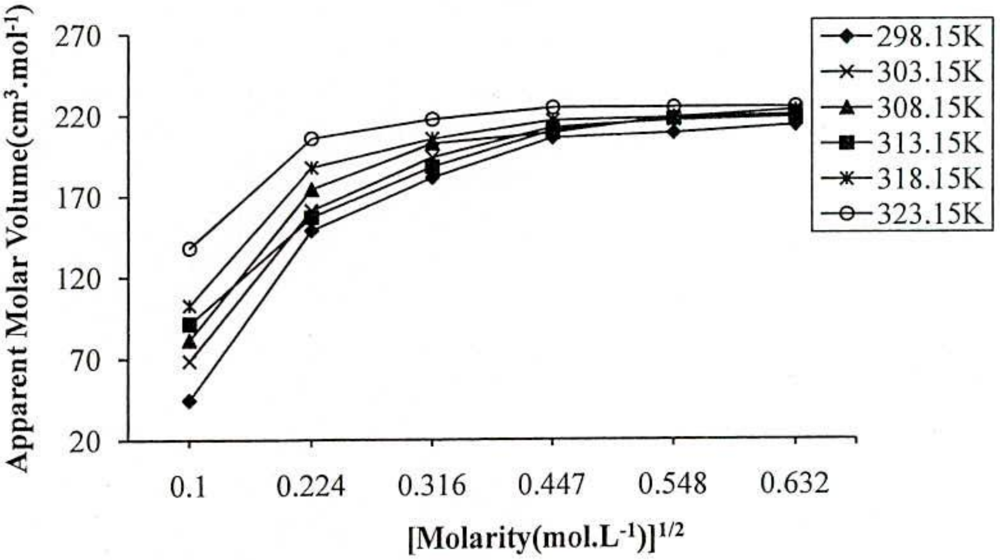


Figure-4.22: Apparent Molar Volume (φ_v) of lauric acid in propanol in presence of 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K

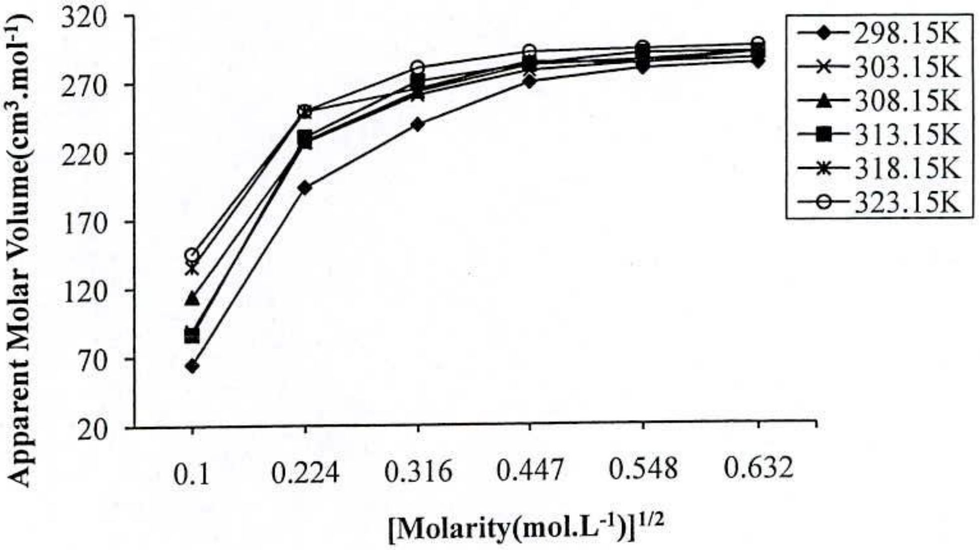


Figure-4.23: Apparent Molar Volume (φ_v) of Palmitic acid in propanol in presence of 0.005 M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K

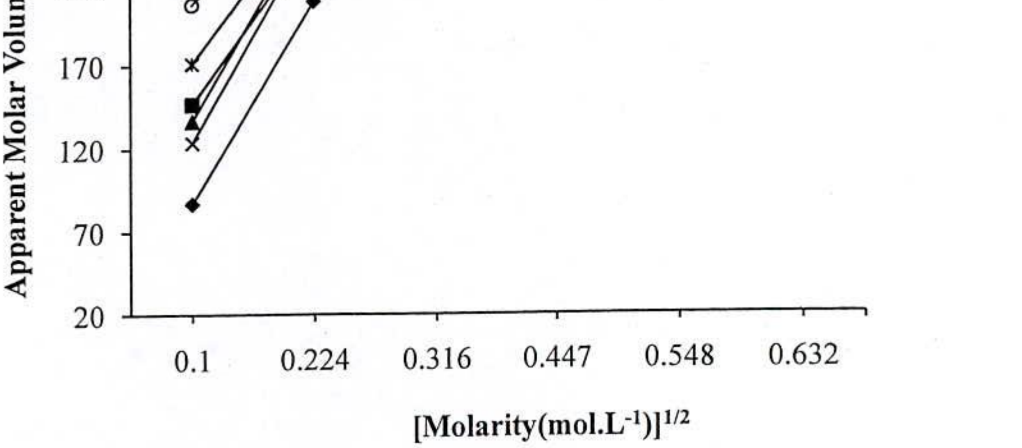


Figure-4.24: Apparent Molar Volume (φ_v) of Stearic acid in propanol in presence of 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K

4.3 Viscometric Properties

The viscosities, η of three fatty acids solutions i.e., lauric, palmitic and stearic acids in propanol at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K over a concentration range of 0.01–0.4 $mol.L^{-1}$ were studied. Results are shown in tables 4.8. The viscosities of the pure propanol at the experimented temperatures are also shown in the table 4.1 for comparison. The values of η of lauric, palmitic and stearic acids in propanol increased with concentration at all six temperatures. The increase of η values of all acids with concentration can be attributed to the increase in both solute–solvent and solute–solute interactions with concentration.

The variation of viscosities with concentration of fatty acids in propanol has been investigated at various temperatures and is shown in figures 4.25-4.27. The following characteristic features of viscosity are observed:

i) Viscosities increased with increasing the concentration fatty acids.

ii) Viscosities decreased with the rise of temperature.

iii) Viscosities increased with increasing the carbon number.

iv) The viscosity maxima follow the order:
Stearic acid – propanol > Palmitic acid – propanol > Lauric acid – propanol

On the other hand, at a constant temperature and concentration, values of η are found to be increased with the carbon number along the hydrocarbon chain of the fatty acid. The increase in η with carbon number can be explained by the increase in both molecular weight of the fatty acid and the degree of solute–solvent interactions with carbon number.

The effect of addition of surfactant, SDS to (fatty acid + propanol) systems has also been studied. The investigated concentrations of SDS were 0.001M and 0.005M. The data of variation of viscosities are presented in table 4.9-4.10. Figures 4.28-4.33 show the plots of corresponding viscosities as well as the effect of addition of SDS to (fatty acid + propanol) systems. From the figures, it is seen that the ultimate pattern of viscosity behavior of lauric, palmitic and stearic acids in SDS solution is very similar to those of propanol systems. The viscosities increased after addition of SDS in comparison to corresponding systems without SDS. The results confer that at molecular arrangements in SDS to (fatty acid + propanol) systems more organized than corresponding systems without SDS and support the density data. This result can be explained in terms of:

i) the establishment of additional hydrophobic interactions among the hydrophobic parts of the surfactant, fatty acids and propanol and

ii) the attainment of solvation through the head group of both solvent and surfactant.

The values of viscosities in SDS systems were found to in the order of:

Alcohol–Fatty acid–0.005 M SDS> Alcohol–Fatty acid–0.001 M SDS>Alcohol–Fatty acid

Table-4.8: Viscosities (mPa.s) of lauric, palmitic and stearic acid in propanol system at 298.15 K, 303.15 K, 308.15 K, 313.15 K, 318.15 K and 323.15K

Name of the system	Conc./ mol.L^{-1}	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
Lauric Acid+ Propanol	0.0100	1.9059	1.6839	1.4559	1.2811	1.1346	0.9996
	0.0500	1.9704	1.7593	1.5585	1.3876	1.2373	1.1072
	0.1000	2.0203	1.7794	1.5774	1.3956	1.2426	1.1045
	0.2000	2.0732	1.8334	1.6285	1.4437	1.2884	1.1440
	0.3000	2.1687	1.9202	1.7030	1.5131	1.3364	1.2015
	0.4000	2.2496	1.9870	1.7540	1.5554	1.3824	1.2435
Palmitic Acid+ Propanol	0.0100	1.9126	1.6910	1.4629	1.2865	1.1405	1.0058
	0.0500	1.9775	1.7930	1.5983	1.4002	1.2611	1.1154
	0.1000	2.0495	1.8101	1.6023	1.4219	1.2699	1.1264
	0.2000	2.1782	1.9276	1.7113	1.5135	1.3591	1.2021
	0.3000	2.3037	2.0437	1.7999	1.5953	1.4227	1.2696
	0.4000	2.4893	2.1961	1.9377	1.7091	1.5265	1.3588
Stearic Acid+ Propanol	0.0100	1.9135	1.6921	1.4639	1.2875	1.1426	1.0091
	0.0500	1.9643	1.7324	1.5348	1.3598	1.2231	1.0781
	0.1000	2.0679	1.8271	1.6074	1.4227	1.2774	1.1256
	0.2000	2.1745	1.9206	1.7054	1.5091	1.3501	1.1986
	0.3000	2.1912	1.9378	1.7247	1.5198	1.3569	1.2006
	0.4000	2.2425	2.0078	1.7326	1.5476	1.375	1.2392

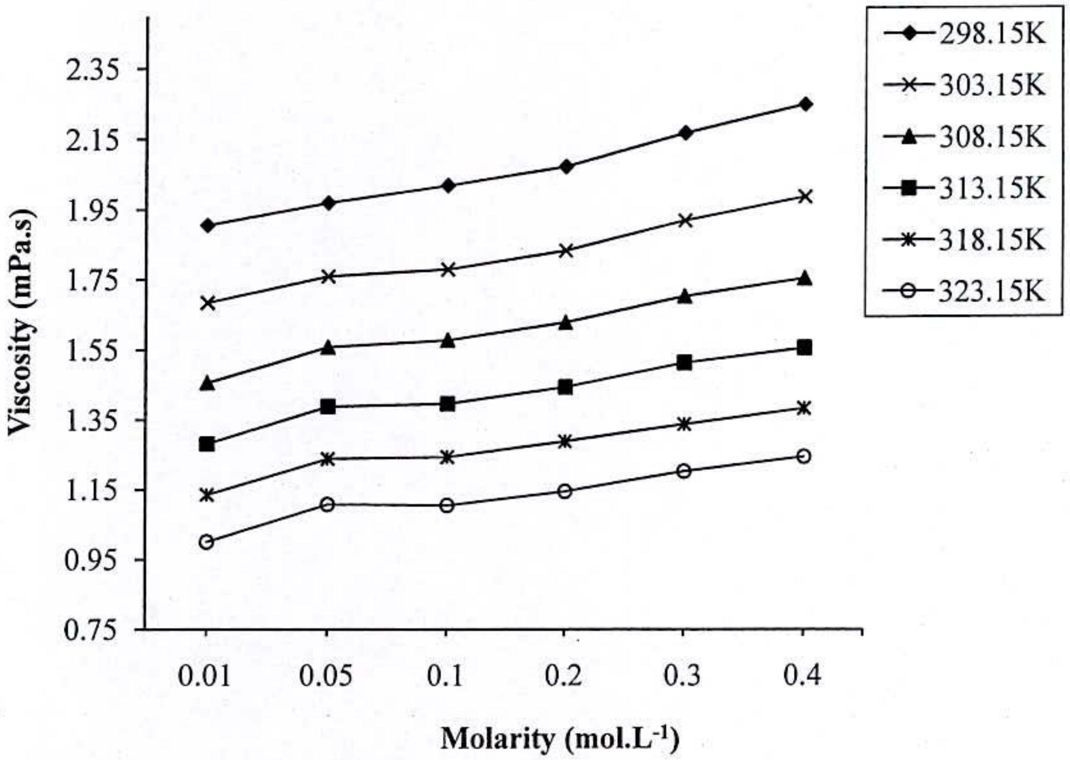


Figure-4.25: Viscosities (η) of lauric acid in propanol at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K

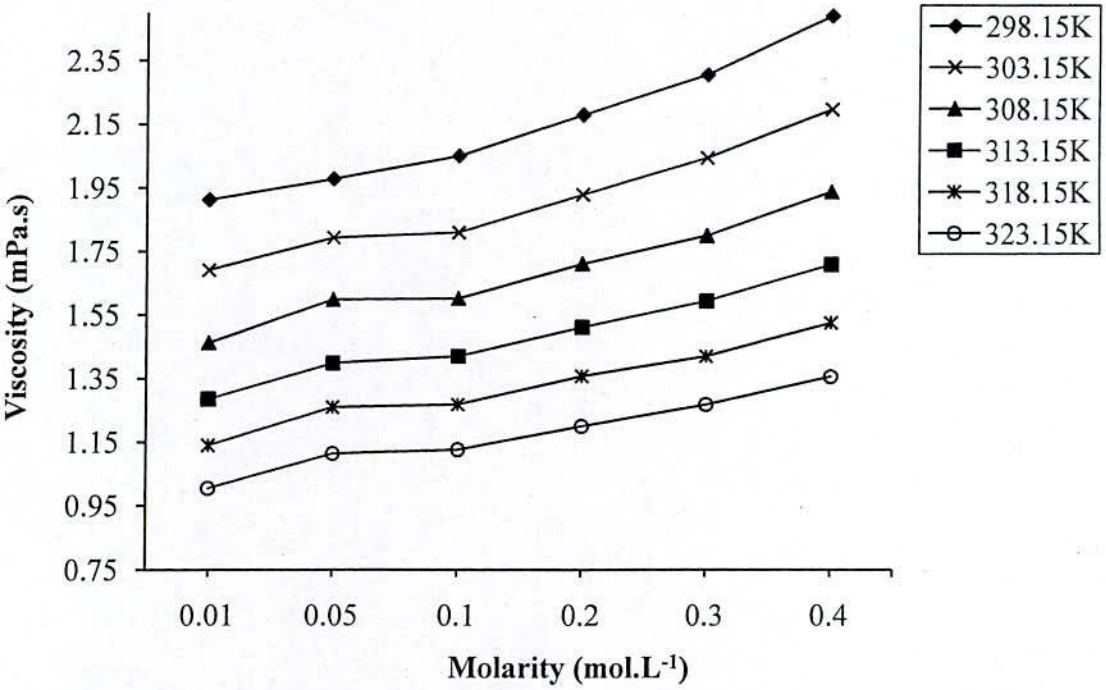


Figure-4.26: Viscosities(η) of Palmitic acid in propanol at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K

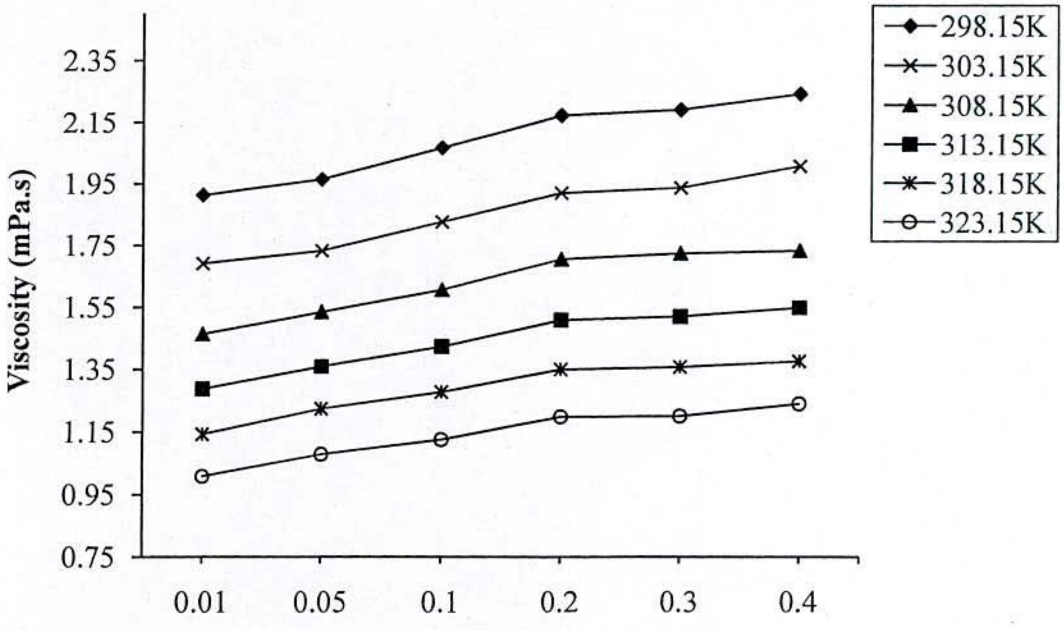


Figure-4.27: Viscosities (η) of Stearic acid in propanol at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K

Table-4.9 : Viscosities (mPa.s) of lauric, palmitic and stearic acid in propanol in presence of 0.001 M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15 K and 323.15K

Name of the system	Conc./ mol.L^{-1}	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
Lauric Acid +Propanol+ 0.001M SDS	0.0100	1.9262	1.6895	1.4621	1.2854	1.1409	1.0055
	0.0500	1.9506	1.7092	1.4778	1.2943	1.1615	1.0164
	0.1000	1.9964	1.7728	1.5712	1.3903	1.2482	1.1033
	0.2000	2.0623	1.8372	1.6078	1.4428	1.2528	1.1475
	0.3000	2.1587	1.9066	1.6880	1.4953	1.3392	1.1844
	0.4000	2.2425	2.0056	1.7490	1.5635	1.4016	1.2345
Palmitic Acid +Propanol+ 0.001M SDS	0.0100	1.9340	1.6921	1.4668	1.2877	1.1442	1.0102
	0.0500	1.9742	1.7307	1.5035	1.3136	1.1843	1.0342
	0.1000	2.0515	1.8174	1.6253	1.4272	1.2761	1.1300
	0.2000	2.0971	1.8705	1.6487	1.4754	1.2912	1.1651
	0.3000	2.2074	1.9784	1.7603	1.5609	1.4323	1.2692
	0.4000	2.2617	2.0426	1.8331	1.6267	1.4777	1.3045
Stearic Acid +Propanol+ 0.001M SDS	0.0100	1.9349	1.6924	1.4676	1.2873	1.1471	1.0217
	0.0500	1.9776	1.7342	1.5119	1.3286	1.1936	1.0384
	0.1000	2.0562	1.8239	1.6175	1.4318	1.2802	1.1305
	0.2000	2.1083	1.8807	1.6592	1.4791	1.3030	1.1745
	0.3000	2.2148	1.9827	1.7653	1.5649	1.4351	1.2718
	0.4000	2.2734	2.0483	1.8444	1.6293	1.4809	1.2892

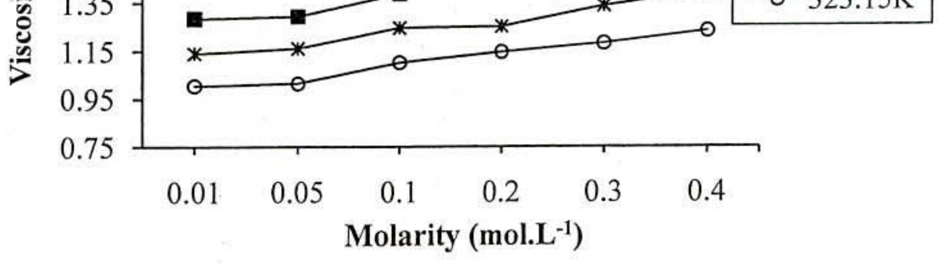


Figure-4.28: Viscosities (η) of lauric acid in propanol in presence of 0.001 M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K

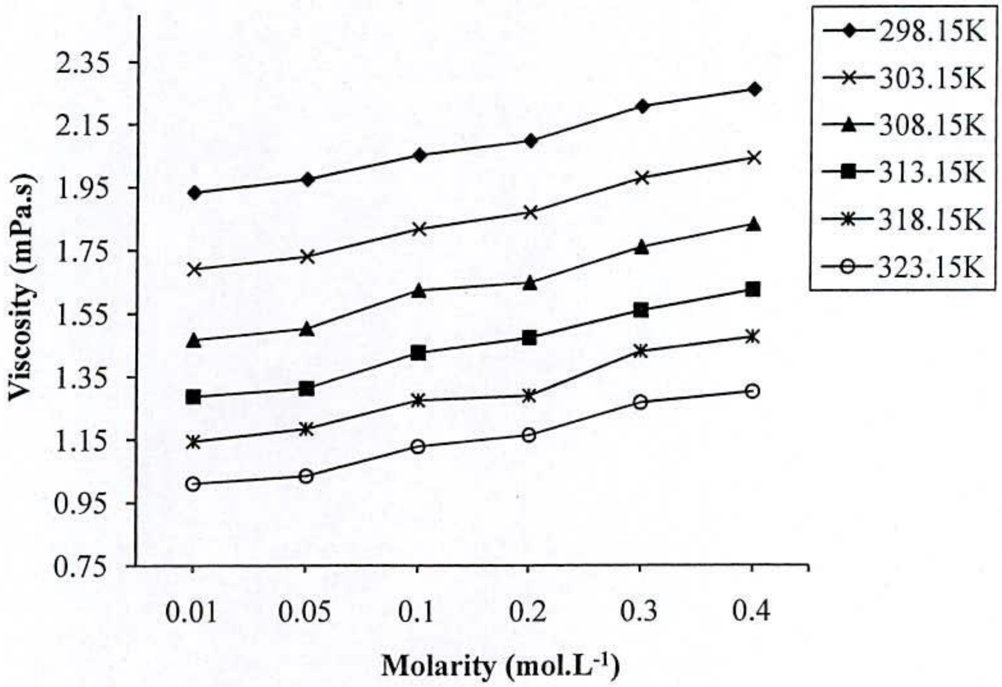


Figure-4.29: Viscosities (η) of palmitic in propanol in presence of 0.001 M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K

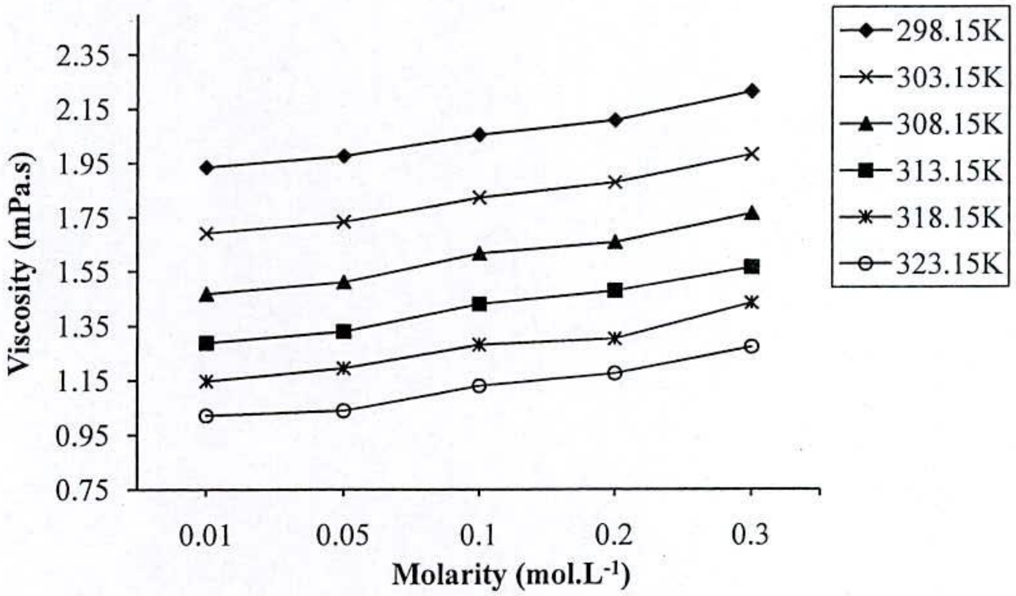


Figure-4.30: Viscosities (η) of Stearic acid in propanol in presence of 0.001 M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K

Table-4.10: Viscosities (mPa.s) of lauric, palmitic and stearic acid in propanol in presence of 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K

Name of the system	Conc./ mol.L^{-1}	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
Lauric Acid +Propanol+ 0.005M SDS	0.0100	1.9349	1.7075	1.4699	1.2897	1.1443	1.0165
	0.0500	1.9702	1.7305	1.5112	1.3354	1.1840	1.0471
	0.1000	2.0099	1.7784	1.5895	1.4078	1.2556	1.1112
	0.2000	2.0955	1.8606	1.6422	1.4655	1.2733	1.1642
	0.3000	2.1502	1.8973	1.6801	1.4891	1.3326	1.1814
	0.4000	2.2617	2.0439	1.7985	1.6005	1.4593	1.2802
Palmitic Acid +Propanol+ 0.005M SDS	0.0100	1.9454	1.7233	1.4791	1.2939	1.1500	1.0229
	0.0500	1.9904	1.7451	1.5340	1.3769	1.1821	1.0627
	0.1000	2.0673	1.8348	1.6194	1.4387	1.2793	1.1347
	0.2000	2.1250	1.8795	1.6740	1.4940	1.3016	1.1796
	0.3000	2.2388	2.0116	1.7894	1.5905	1.4539	1.2729
	0.4000	2.2809	2.0608	1.8553	1.6457	1.5067	1.3097
Stearic Acid +Propanol+ 0.005M SDS	0.0100	1.9470	1.7375	1.4813	1.2969	1.1545	1.0456
	0.0500	1.9982	1.7544	1.5609	1.3990	1.2400	1.0839
	0.1000	2.0896	1.8452	1.6357	1.4501	1.2944	1.1460
	0.2000	2.1527	1.8925	1.6889	1.5129	1.3184	1.1892
	0.3000	2.2510	2.0194	1.7959	1.6043	1.4615	1.2758
	0.4000	2.2925	2.0803	1.8738	1.6463	1.5269	1.3204

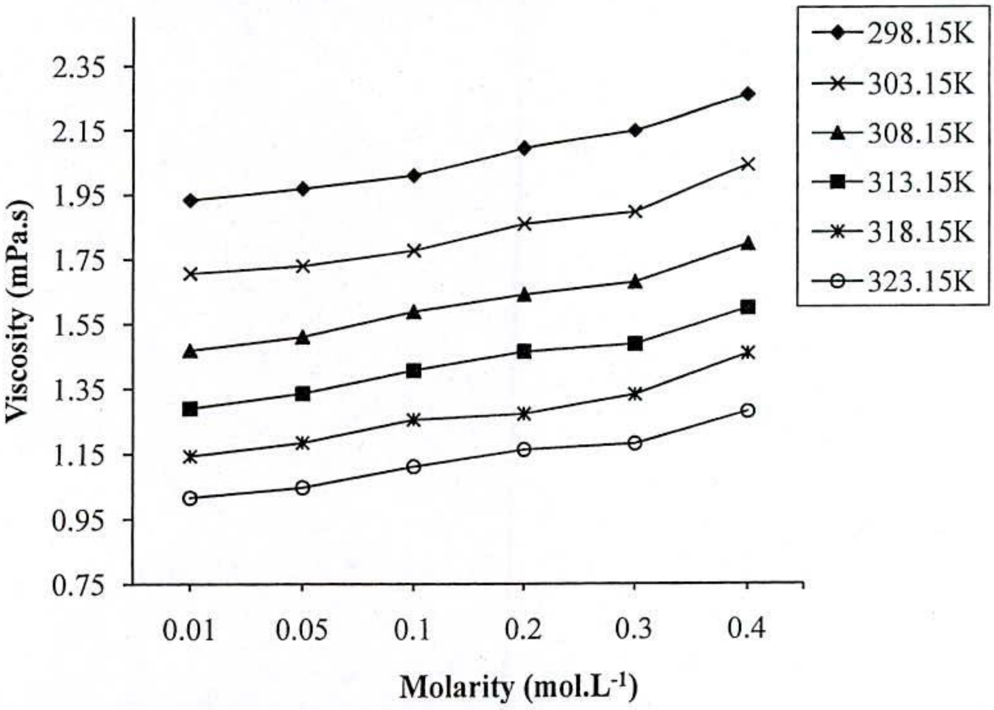


Figure-4.31: Viscosities(η) of lauric acid in propanol in presence of 0.005 M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K

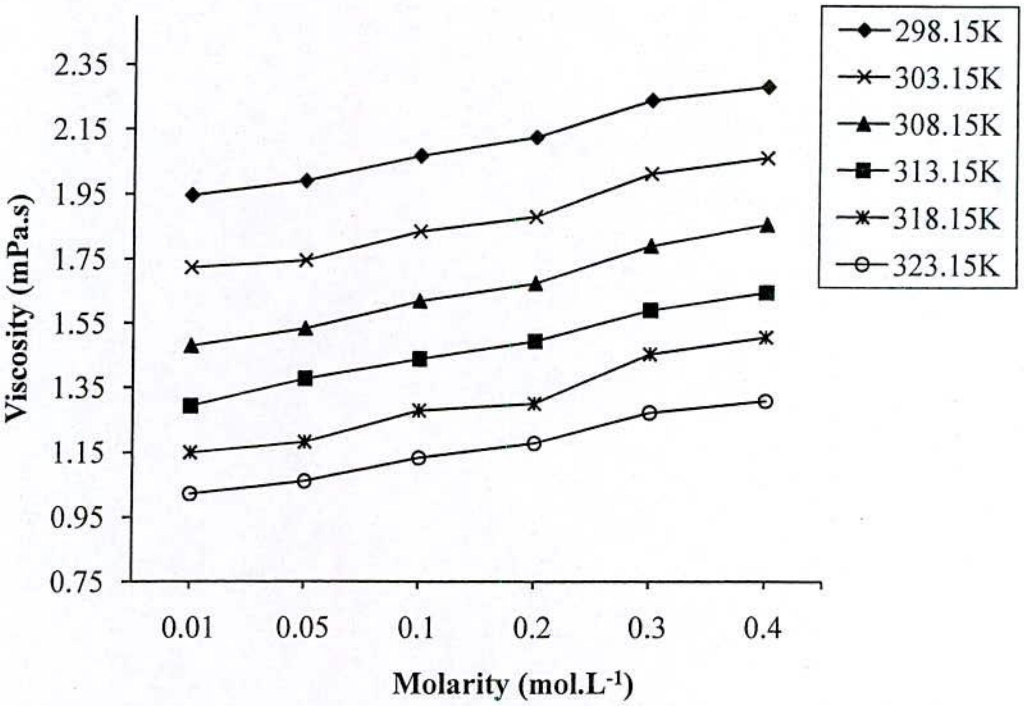


Figure-4.32: Viscosities(η) of Palmitic acid in propanol in presence of 0.005 M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K

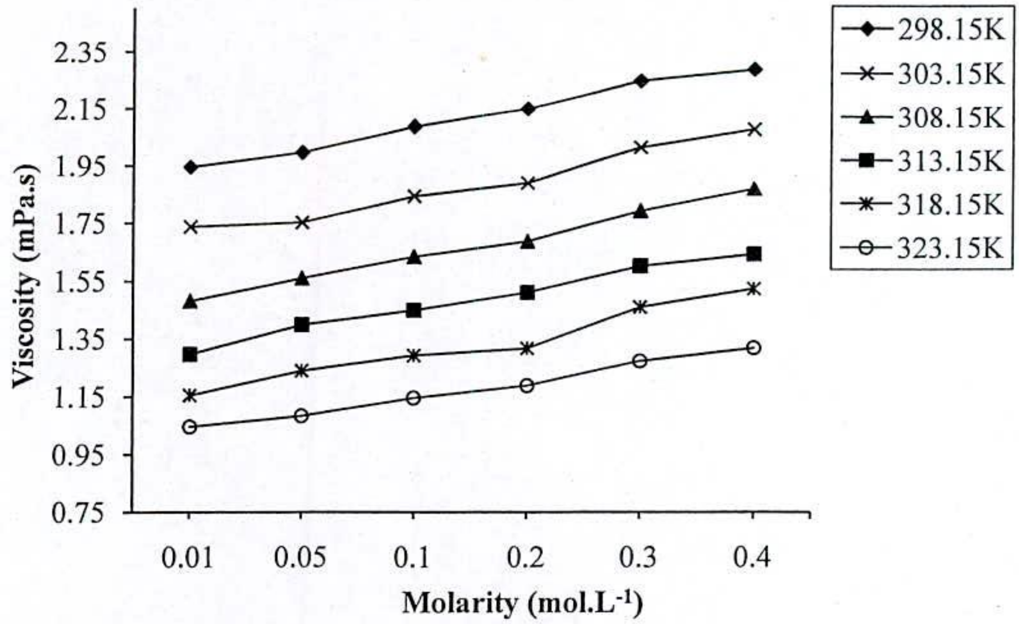


Figure-4.33: Viscosities(η) of Stearic acid in propanol in presence of 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K

4.4 Thermodynamic Properties

Thermodynamic properties, free energy, ΔG*, change of enthalpy, ΔH* and entropy, ΔS* for viscous flow have been calculated from viscometric data. The ΔG* values are positive for all the studied systems indicate that the studied systems are non-spontaneous, i.e., work has to be done to overcome the energy barrier for the viscous flow process as shown in table **4.11-4.13.** The ΔH* values are positive for all the studied systems indicate that work has to be done to overcome the energy barrier for the flow process as shown in table 4.14-4.16. That is, the viscous flow is not thermodynamically favored for the systems studied. The value of entropy of activation, ΔS* of the investigated systems are shown in table 4.14-4.16. The ΔS* values are negative for all the systems studied. Negative values of the mixtures indicate that these are more ordered or structured than the pure propanol.

Table-4.11: Free energy, ΔG* (KJ.mol^{-1}) of lauric, palmitic and stearic acid in propanol system at 298.15 K, 303.15 K, 308.15 K, 313.15 K, 318.15 K and 323.15 K

Name of the system	Conc./ mol.L^{-1}	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
Lauric Acid+ Propanol	0.0100	68.92	69.77	70.56	71.38	72.22	73.02
	0.0500	69.00	69.88	70.73	71.59	72.44	73.30
	0.1000	69.07	69.91	70.76	71.61	72.46	73.29
	0.2000	69.13	69.98	70.85	71.70	72.55	73.39
	0.3000	69.24	70.10	70.96	71.82	72.65	73.52
	0.4000	69.33	70.19	71.04	71.89	72.74	73.61
Palmitic Acid+ Propanol	0.0100	69.54	70.40	71.20	72.04	72.88	73.70
	0.0500	69.62	70.55	71.43	72.26	73.15	73.98
	0.1000	69.71	70.57	71.43	72.30	73.16	74.01
	0.2000	69.86	70.73	71.60	72.46	73.34	74.18
	0.3000	70.00	70.88	71.73	72.60	73.47	74.33
	0.4000	70.19	71.06	71.92	72.78	73.65	74.51
Stearic Acid+ Propanol	0.0100	69.80	70.66	71.47	72.31	73.16	73.99
	0.0500	69.86	70.72	71.59	72.45	73.34	74.17
	0.1000	69.99	70.86	71.71	72.57	73.45	74.28
	0.2000	70.12	70.98	71.86	72.72	73.60	74.45
	0.3000	70.13	71.00	71.89	72.74	73.61	74.46
	0.4000	70.19	71.09	71.90	72.79	73.65	74.54

Table-4.12: Free energy, ΔG^* (KJ.mol^{-1}) of lauric, palmitic and stearic acid in propanol in presence of 0.001M SDS system at 298.15 K, 303.15 K, 308.15 K, 313.15 K, 318.15 K and 323.15 K

Name of the system	Conc./mol.L^{-1}	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
Lauric Acid +Propanol+0.001M SDS	0.0100	68.95	69.78	70.57	71.39	72.23	73.04
	0.0500	68.98	69.81	70.60	71.41	72.28	73.07
	0.1000	69.04	69.90	70.75	71.60	72.47	73.29
	0.2000	69.12	69.99	70.81	71.69	72.48	73.39
	0.3000	69.23	70.08	70.94	71.79	72.65	73.48
	0.4000	69.32	70.21	71.03	71.90	72.77	73.59
Palmitic Acid +Propanol+0.001M SDS	0.0100	69.57	70.40	71.21	72.04	72.89	73.71
	0.0500	69.62	70.46	71.27	72.09	72.98	73.78
	0.1000	69.71	70.58	71.47	72.31	73.18	74.01
	0.2000	69.77	70.65	71.51	72.39	73.21	74.10
	0.3000	69.90	70.79	71.67	72.54	73.48	74.33
	0.4000	69.96	70.88	71.78	72.65	73.56	74.40
Stearic Acid +Propanol+0.001M SDS	0.0100	69.83	70.66	71.48	72.31	73.17	74.02
	0.0500	69.88	70.73	71.55	72.39	73.28	74.07
	0.1000	69.98	70.85	71.73	72.58	73.46	74.30
	0.2000	70.04	70.93	71.79	72.67	73.51	74.40
	0.3000	70.16	71.06	71.95	72.82	73.76	74.61
	0.4000	70.23	71.14	72.06	72.92	73.85	74.65

Table-4.13: Free energy, ΔG^* (KJ.mol^{-1}) of lauric, palmitic and stearic acid in propanol in presence of 0.005 M SDS system at 298.15 K, 303.15 K, 308.15 K, 313.15 K, 318.15 K and 323.15 K

Name of the system	Conc./mol.L^{-1}	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
Lauric Acid +Propanol+0.005M SDS	0.0100	68.96	69.80	70.58	71.40	72.24	73.07
	0.0500	69.00	69.84	70.65	71.49	72.33	73.15
	0.1000	69.05	69.91	70.78	71.63	72.48	73.31
	0.2000	69.15	70.02	70.87	71.73	72.52	73.43
	0.3000	69.22	70.07	70.92	71.77	72.64	73.47
	0.4000	69.34	70.26	71.10	71.96	72.88	73.69
Palmitic Acid +Propanol+0.005M SDS	0.0100	69.58	70.45	71.23	72.05	72.90	73.75
	0.0500	69.64	70.48	71.32	72.21	72.97	73.85
	0.1000	69.73	70.61	71.46	72.33	73.18	74.03
	0.2000	69.80	70.67	71.55	72.42	73.23	74.13
	0.3000	69.93	70.84	71.72	72.59	73.52	74.33
	0.4000	69.98	70.90	71.81	72.68	73.62	74.41
Stearic Acid +Propanol+0.005M SDS	0.0100	69.84	70.73	71.50	72.33	73.19	74.09
	0.0500	69.90	70.75	71.63	72.52	73.38	74.18
	0.1000	70.02	70.88	71.75	72.62	73.49	74.33
	0.2000	70.09	70.94	71.84	72.73	73.54	74.43
	0.3000	70.20	71.11	71.99	72.88	73.81	74.62
	0.4000	70.25	71.18	72.10	72.95	73.93	74.71

Table-4.14: ΔH^* and ΔS^* for lauric, palmitic and stearic acid in propanol system at 298.15 K, 303.15 K, 308.15 K, 313.15 K, 318.15 K and 323.15 K

Name of the system	Temperature	ΔH^*(KJ.mol^{-1})	ΔS^*(mol^{-1})
Lauric Acid + Propanol	298.15K	20.06	-0.16
	303.15K	17.84	-0.17
	308.15K	18.60	-0.17
	313.15K	18.29	-0.17
	318.15K	18.32	-0.17
	323.15K	18.39	-0.17
Palmitic Acid + Propanol	298.15K	19.99	-0.17
	303.15K	17.81	-0.17
	308.15K	18.39	-0.17
	313.15K	18.24	-0.17
	318.15K	18.44	-0.17
	323.15K	18.71	-0.17
Stearic Acid + Propanol	298.15K	19.91	-0.17
	303.15K	18.34	-0.17
	308.15K	18.67	-0.17
	313.15K	18.31	-0.17
	318.15K	18.52	-0.17
	323.15K	18.58	-0.17

Table-4.15: $\Delta H^*$and ΔS^* for lauric ,palmitic and stearic acid in propanol in presence of 0.001M SDS system at 298.15 K, 303.15 K, 308.15 K, 313.15 K, 318.15 K and 323.15 K

Name of the system	Temperature	ΔH^*(KJ.mol^{-1})	ΔS^*(mol^{-1})
Lauric Acid +Propanol+.001M SDS	298.15K	20.15	-0.16
	303.15K	20.12	-0.16
	308.15K	18.23	-0.17
	313.15K	18.46	-0.17
	318.15K	18.43	-0.17
	323.15K	18.38	-0.17
Palmitic Acid +Propanol+.001M SDS	298.15K	20.13	-0.17
	303.15K	19.92	-0.17
	308.15K	18.39	-0.17
	313.15K	18.34	-0.17
	318.15K	16.95	-0.18
	323.15K	16.87	-0.18
Stearic Acid +Propanol+.001M SDS	298.15K	19.84	-0.17
	303.15K	19.74	-0.17
	308.15K	18.38	-0.17
	313.15K	18.23	-0.17
	318.15K	16.96	-0.18
	323.15K	17.26	-0.18

Table-4.16: ΔH^* and ΔS^* for lauric, palmitic and stearic acid in propanol in presence of 0.005M SDS system at 298.15 K, 303.15 K, 308.15 K, 313.15 K, 318.15 K and 323.15 K

Name of the system	Temperature	ΔH^* (KJ.mol^{-1})	ΔS^* (mol^{-1})
Lauric Acid +Propanol+.001M SDS	298.15K	20.12	-0.16
	303.15K	19.53	-0.17
	308.15K	18.17	-0.17
	313.15K	18.47	-0.17
	318.15K	18.39	-0.17
	323.15K	17.46	-0.17
Palmitic Acid +Propanol+.001M SDS	298.15K	20.17	-0.17
	303.15K	19.49	-0.17
	308.15K	18.50	-0.17
	313.15K	18.32	-0.17
	318.15K	17.20	-0.18
	323.15K	16.81	-0.18
Stearic Acid +Propanol+.001M SDS	298.15K	19.74	-0.17
	303.15K	18.53	-0.17
	308.15K	18.44	-0.17
	313.15K	18.32	-0.17
	318.15K	17.22	-0.18
	323.15K	16.723	-0.180

Table-4.17: Densities (ρ) of propanol + SDS at 298.15 K, 303.15 K, 308.15 K, 313.15 K, 318.15 K and 323.15K

Temperature	Density (g.cm^{-3})	
	propanol + 0.001M SDS	propanol + 0.005M SDS
298.15K	0.803706	0.803655
303.15K	0.802500	0.802448
308.15K	0.798902	0.798847
313.15K	0.794871	0.794822
318.15K	0.791060	0.791009
323.15K	0.787136	0.787082

CHAPTER V

Conclusion

Volumetric, viscometric and thermodynamic properties of some fatty acids e.g., lauric, palmitic and stearic acids were studied in propanol and also in (propanol + SDS). All the fatty acids are found to be dissolved in propanol over a concentration range of 0.01–0.4 mol.L^{-1}. The effect of addition of surfactant, SDS to (fatty acid + propanol) systems has also been studied. The investigated concentrations of SDS were 0.001M and 0.005 M. Some interesting solution properties of these fatty acids in different systems were observed as follows:

(i) Volumetric, viscometric and thermodynamic properties are depended upon fatty acids concentration as well as on the temperature.

(ii) The apparent molar volume, $\boldsymbol{\varphi_v}$ values increased at all concentrations and temperatures exponentially for all three fatty acids both in fatty acid–propanol and fatty acid–propanol–SDS systems.

(iii) The apparent molar volume, $\boldsymbol{\varphi_v}$ values increased with increasing chain length of the fatty acids.

(iv) The viscosities, η values increased with concentration but decreased with temperature for all three fatty acids both in fatty acid–propanol and fatty acid–propanol–SDS systems.

(v) The viscosities, η values were also found to be increased with increasing the carbon numbers of the fatty acids.

(vi) The change of free energy, **ΔG*** and enthalpy ,**ΔH*** values for viscous flow are found to be positive for all the studied systems indicate that work has to be done to overcome the energy barrier for the flow process. The change of entropy, **ΔS*** values for the flow process are negative indicating the studied systems are more structured.

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