Thermodynamic Characterization of Anionic Surfactants in Binary Solvent Systems Across Different Temperatures

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Abstract:
Anionic surfactants, Sodium Stearate (SS), Potassium Stearate (PS), Sodium Oleate (SO) and Sodium Laulryl Sulphate (SLS) in binary alcohol-water solvent systems of varying composition have been studied at various mole fractions of the salts at various temperatures through conductivity measurements. The CMC value of anionic surfactants is seen to be increased with the rising of temperatures in alcohols-water systems. Thermodynamic parameters Enthalpy (ΔH°_{m}), Entropy (ΔS°_{m}) and Free energy (ΔG°_{m}) of micellization of anionic surfactants Sodium Stearate, Potassium Stearate, Sodium Oleate and Sodium Laulryl Sulphate have been determined in the varying composition of alcohol-water solvent systems at 303 K, 308 K, 313 K and 318 K. Different thermodynamic parameters have been reported.

Keywords: anionic surfactants, thermodynamic parameters, critical micelle concentration (CMC), conductivity (k).

INTRODUCTION

Anionic surfactants, Sodium Stearate(SS), Potassium Stearate(PS), Sodium Oleate(SO) and Sodium Laulryl Sulphate(SLS) play a very important role in human life.

The molecular formula of Sodium Stearate is $C_{18}H_{35}NaO_2$. Reactive Sodium Stearate grease systems are broadly utilized as a part of the metal shaping and metal working industry, particularly in cool framing tasks [1]. Such responsive Sodium Stearate grease systems comprise of high-virtue sodium stearate in a aqueous solution and are regularly referred to just as "receptive cleansers [2]. Such responsive cleansers have been utilized as a part of metal treating tasks for in any event the last forty years [3]. The responsive cleansers for cold shaping activities are set up from high immaculateness stearic acid which contains around 95 percent by weight, at the very least, of the C-18 greasy acid and just low levels of substantial metals [4]. Generally, a receptive cleanser shower contains around one pound of Sodium Stearate per gallon of shower. In light of the broad utilization of such showers in cold framing of steel and aluminum, the cost of high virtue Sodium Stearate represents to a considerable cost component in cool shaping tasks [5].

Atomic Formula of Potassium Stearate is $C_{18}H_{35}KO_2$ and it is additionally gotten from Stearic Acid—a result of vegetable oil through the saponification procedure. Potassium Stearate is basically utilized as a purifying operator and emulsifier. It is found in numerous individual care and cosmetic applications. It can likewise be utilized as a part of some elastic assembling and as a base for material conditioners [6].

Sodium Oleate $C_{18}H_{33}O_2Na$ is the sodium salt of oleic acid, a monounsaturated unsaturated fatty acid. This anionic surfactant and emulsifier is a part of industrial cleansers. The impact of Sodium Oleate and different emulsifiers has been examined in the crystallization temperature and polymorphism of tripalmitin nano-particles in colloidal dispersions [7]. The constancy of the compound Prolidase has been researched in poly(lactide-co-glycolide) miniaturized scale particulate details that incorporate Sodium Oleate as an emulsifier.

Sodium Lauryl Sulfate(SLS) synonymously Sodium Dodecyl Sulfate (SDS), Sodium Lauryl Sulfate is a manufactured organic compound with the formula $CH_3(CH_2)_{11}SO_4Na$. It is an ionic surfactant utilized as a part of numerous cleaning and cleanliness items. The sodium salt is of an organo sulphate class of organics [8]. SLS has been proposed as a conceivably compelling topical microbicide, for intravaginal use, to hinder and potentially avoid contamination by different wrapped and non-encompassed infections, for example, the herpes simplex infections, HIV and the Semliki Forest infection [9, 10].

The study of thermodynamic properties is very important to study the interaction between solute and solute as well as between solute and solvent molecules. Moreover the use of a liquid mixture as a solvent instead of a single liquid is superior as it contains the basic properties of the two liquids.In the present paper thermodynamic properties Enthalpy (ΔH°_{m}), Entropy (ΔS°_{m}) and Free energy (ΔG°_{m}) of micellization of anionic surfactants Sodium Stearate, Potassium Stearate, Sodium Oleate and Sodium Laulryl Sulphate have been determined in the varying composition of alcohol-water solvent systems at 303 K, 308 K, 313 K and 318 K.

Experimental Procedure Materials

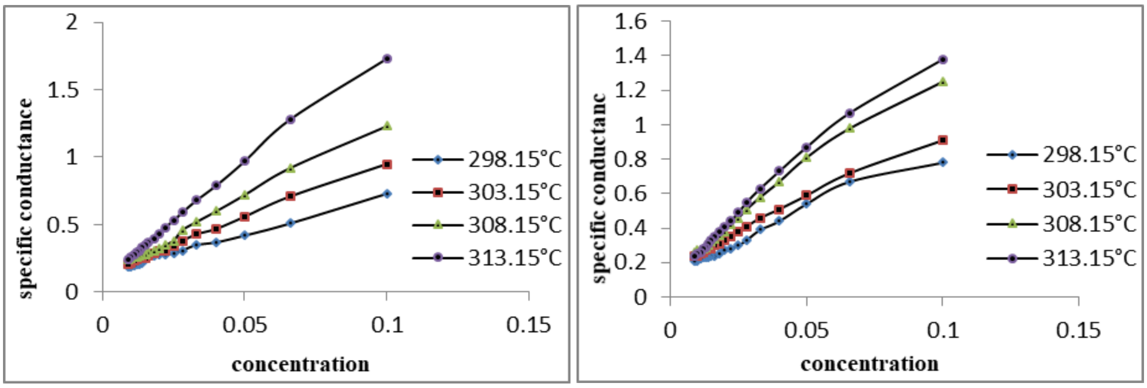
The anionic surfactants, Sodium Stearate(SS, 98.0% CDH central drug house (P) Ltd.),Potassium Stearate(PS, 98%CDH), Sodium Oleate(SO, 98%CDH) and Sodium Laulryl Sulphate(SLS, 90%CDH) were used as formerly described. All solutions have been prepared using alcohol and conductivity water. Conductivity water was obtained by initially distilling distilled water with acidified $KMnO_4$ and later with tiny amount of NaOH pellets and resulting vapours were condensed and collected as conductivity water. Potassium Hydroxide was used to purify alcohol by keeping over it for a day and distilled. The distillate was refluxed with 1% of Calcium metal for about eight hours and then redistilled. Only analytical grade reagents were used.

Conductance Methods

Keroy digital balance was utilised in preparation of the solutions. The concentration of pioneer solution was kept 0.1 N and successive solutions were prepared by dilution method in each solvent. The solutions have been kept for ten minutes at desired temperature earlier than use. Conductivity measurements were made using a CM 180 Digital Conductivity Meter geared up with a dip cellular (cell constant $0.99cm^{-1}$) and the calibration of the device was made with 0.01 M KCL solutions at usual time durations.

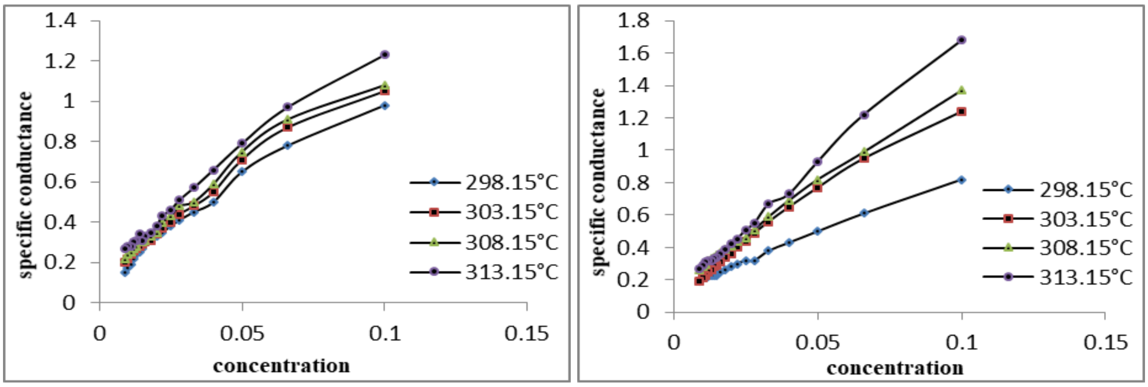
Results and Discussion

The specific conductance of the SS, PS, SO and SLS solutions were found out from the conductance measurements of the solutions in the pure solvents as well as in the alcohol-water systems at temperatures303 K, 308 K, 313 K and 318 K. The variation in conductance values of the solutions are observed in the various solvent systems made up of alcohol and water in various compositions at different temperatures. The CMCs of the solutions were determined using classical methods.



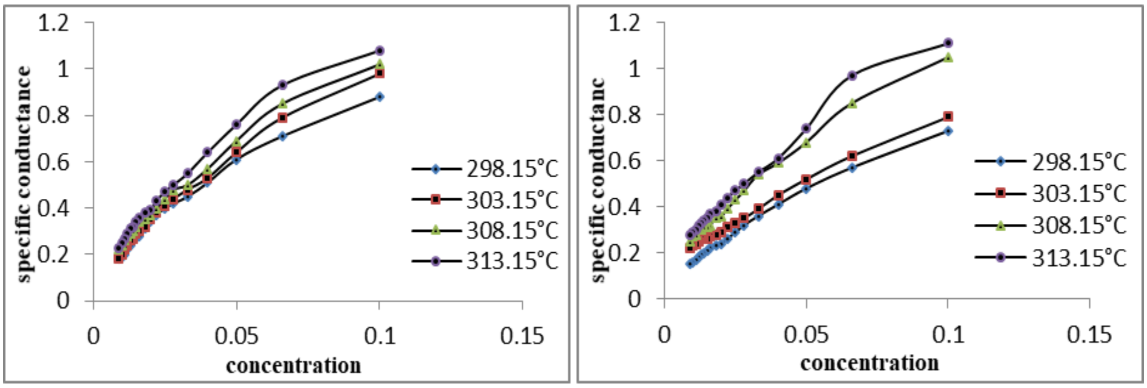
(a) **(b)**

Fig 1: Plots of specific conductance vs. concentration of (a) Sodium Stearate and (b) Potassium Stearate in 80% alcohol system at various temperatures.



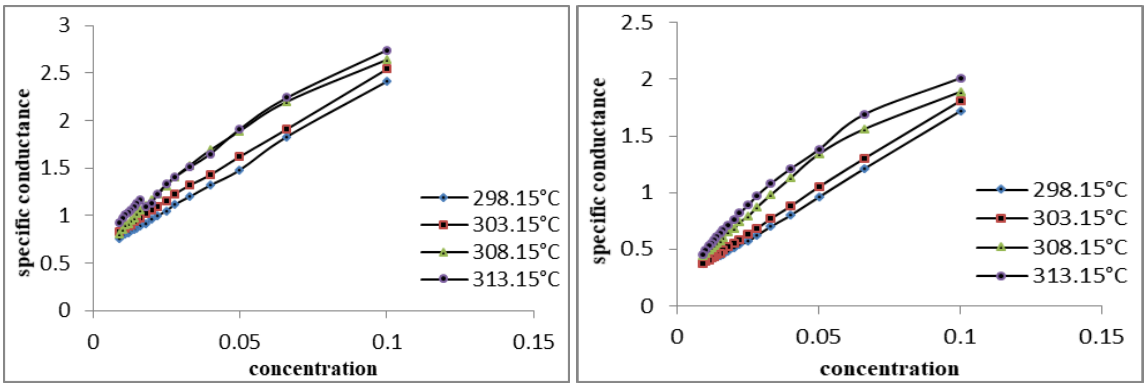
(a) **(b)**

Fig 2: Plots of specific conductance vs. concentration of (a) Sodium Stearate and (b) Potassium Stearate in 90% alcohol system at various
temperatures

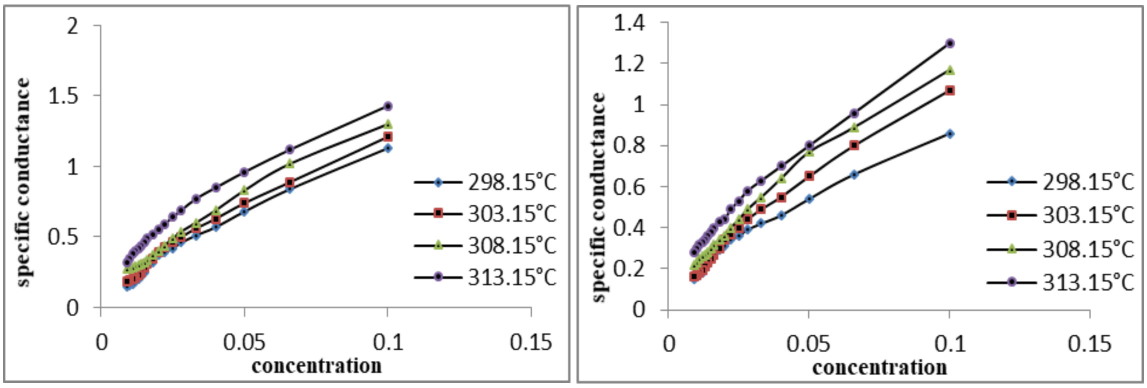


(a) **(b)**

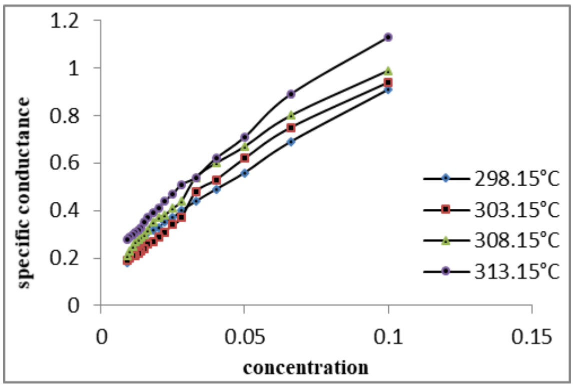
Fig 3: Plots of specific conductance vs. concentration of (a) Sodium Stearate and (b) Potassium Stearate in 100% alcohol system at various temperatures.



(a) **(b)**



(c) **(d)**



(e)

Fig 4: Plots of specific conductance vs. concentration of Sodium Lauryl Sulphate (SLS) in (a) 0% alcohol system (b) 50% alcohol system (c)80% alcohol system (d) 90% alcohol system (e) 100% alcohol system at various temperatures.

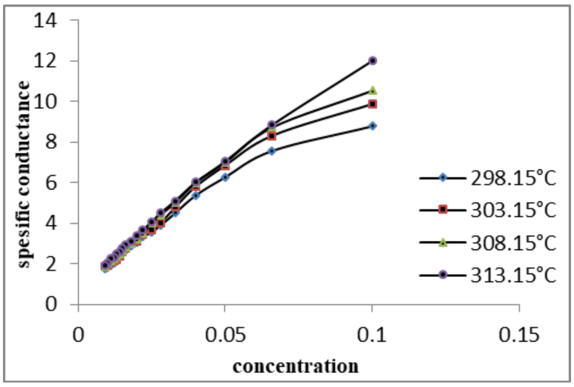


Fig 5: Plot of specific conductance vs. concentration for Sodium Oleate in 0% alcohol at various temperatures.

The plots of specific conductance verses concentration for SS and PS in 80%, 90%, 100% Alcohol-Water solvent systems are presented in fig. 1and 2 while in pure water is presented in fig. 3 or 4 shows plots of specific conductance vs. concentration for Sodium Lauryl Sulphate (SDS) in (a) 0% alcohol system (b) 50% alcohol system (c) 80% alcohol system (d) 90% alcohol system and (e) 100% alcohol system at various temperatures. Fig. 5 shows plot of specific conductance vs. concentration for Sodium Oleate in 0% alcohol at various temperatures.

From these plots the CMC values are found out. The conductivity is seen to be increased with increasing concentration in each case. But after CMCs the rate of increase of conductivity is lesser than that at before CMCs. This can be explained by the very fact that beyond the CMC, condensation counter-ions are formed on the micelles, causing a decrease in the number of charge carriers and hence the conductivity decreases slightly. The CMC values are also observed to be increased with increase in temperature in each case. The values of CMC are presented in Table 1.

The thermodynamic parameters standard Gibbs free energy of micellization ($\Delta G_m°$), standard enthalpy of micellization ($\Delta H_m°$), standard entropy ($\Delta S_m°$) of micellization and variation in heat capacity ($\Delta C_p°$) of surfactants in the solvent systems made from alcoholic and aqueous solutions $\Delta C_p° = (\Delta H°m/\Delta T)$ *4*

$$\frac{\Delta Hm° - \Delta Sm°}{T}$$

Where T is the absolute temperature, R is the universal gas constant and CMC is the critical micelle concentration.

Table 1: CMC values (mol/l) for Sodium Stearate(SS), Potassium Stearate(PS), Sodium Oleate(SO) and Sodium Laulryl Sulphate(SLS)in alcohol-water systems at different temperatures.

System	Temperature (K)	0% alcohol	50% alcohol	80% alcohol	90% alcohol	100% alcohol
SDS	298.15	0.016	0.016	0.020	0.022	0.018
	303.15	0.018	0.020	0.022	0.025	0.020
	308.15	0.022	0.025	0.025	0.028	0.022
	313.15	0.025	0.033	0.028	0.033	0.025
Sodium Stearate	298.15	-----	-----	0.018	0.020	0.018
	303.15	-----	-----	0.022	0.022	0.020
	308.15	-----	-----	0.025	0.028	0.025
	313.15	-----	-----	0.033	0.033	0.028
Potassium Stearate	298.15	-----	-----	0.018	0.020	0.018
	303.15	-----	-----	0.020	0.022	0.020
	308.15	-----	-----	0.028	0.028	0.022
	313.15	-----	-----	0.033	0.033	0.028
Sodium Oleate	298.15	0.016	-----	-----	-----	-----
	303.15	0.020	-----	-----	-----	-----
	308.15	0.022	-----	-----	-----	-----
	313.15	0.028	-----	-----	-----	-----

Critical micelle concentrations (CMC) of anionicat surfactants considerably increase in alcoholic aqueous solutions at various temperatures. CMC value depends upon the surfactant particle structure and is affected by the presence of inorganic salts in the scattering medium. CMC value must be known in numerous utilizations of surfactants like detergency and colloid adjustments [4].

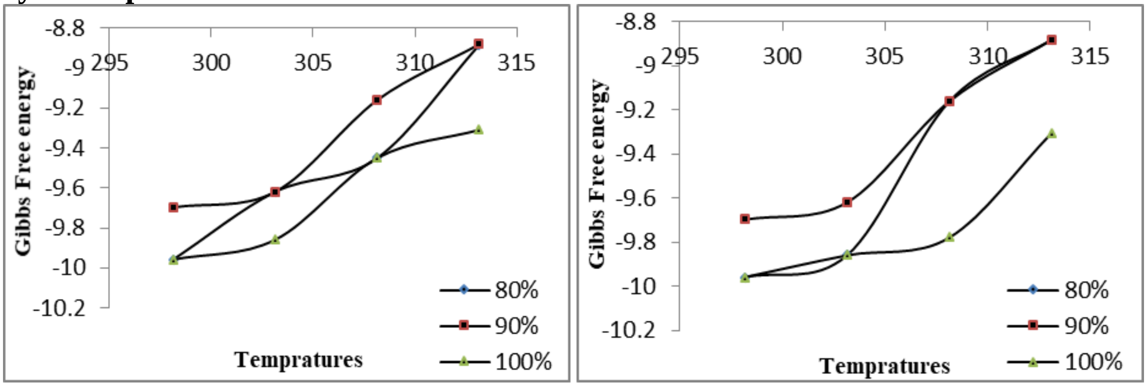
Thermodynamic parameters

different temperatureswere calculated using andequation1,2,3and 4 [11, 12,13, 14].

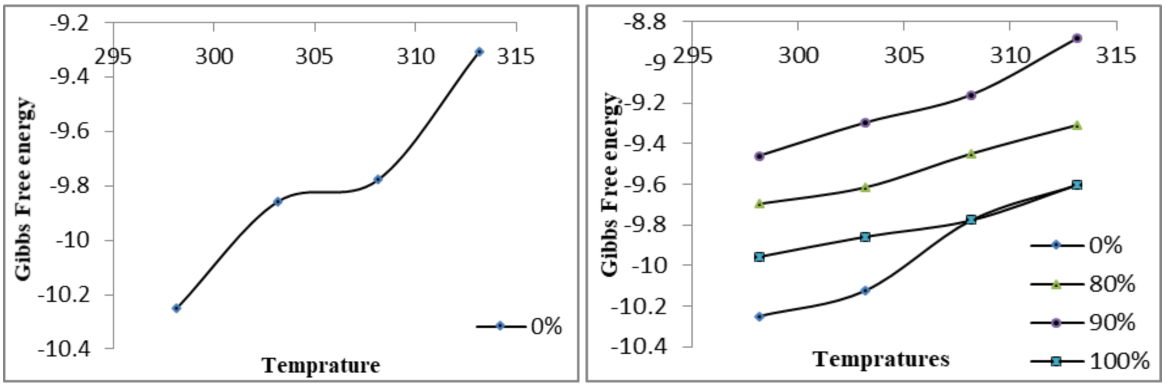
$$\Delta G_m^\circ = RT\ln X_{CMC} \quad ....1$$

$$\Delta H_m^\circ = -RT^2 \frac{d\ln X_{cmc}}{dT} \quad ....2$$

$$\Delta S_m^\circ = \quad ....3$$

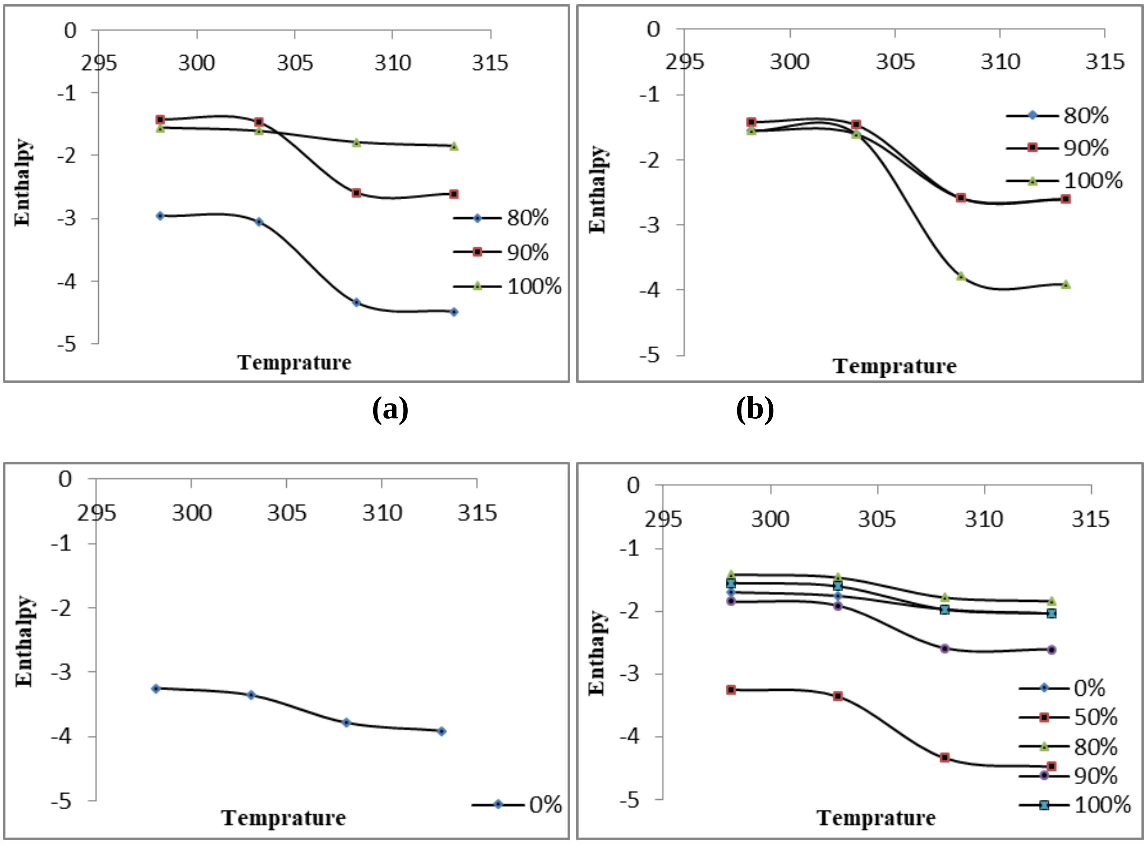


(a) (b)



(c) **(d)**

Fig 6: Plots of gibbs free energy of micellization vs. Temperature for (a) Sodium Stearate (b) Potassium Stearate (c) Sodium Oleate and (d) SLS in different alcohol water-systems at various temperatures.

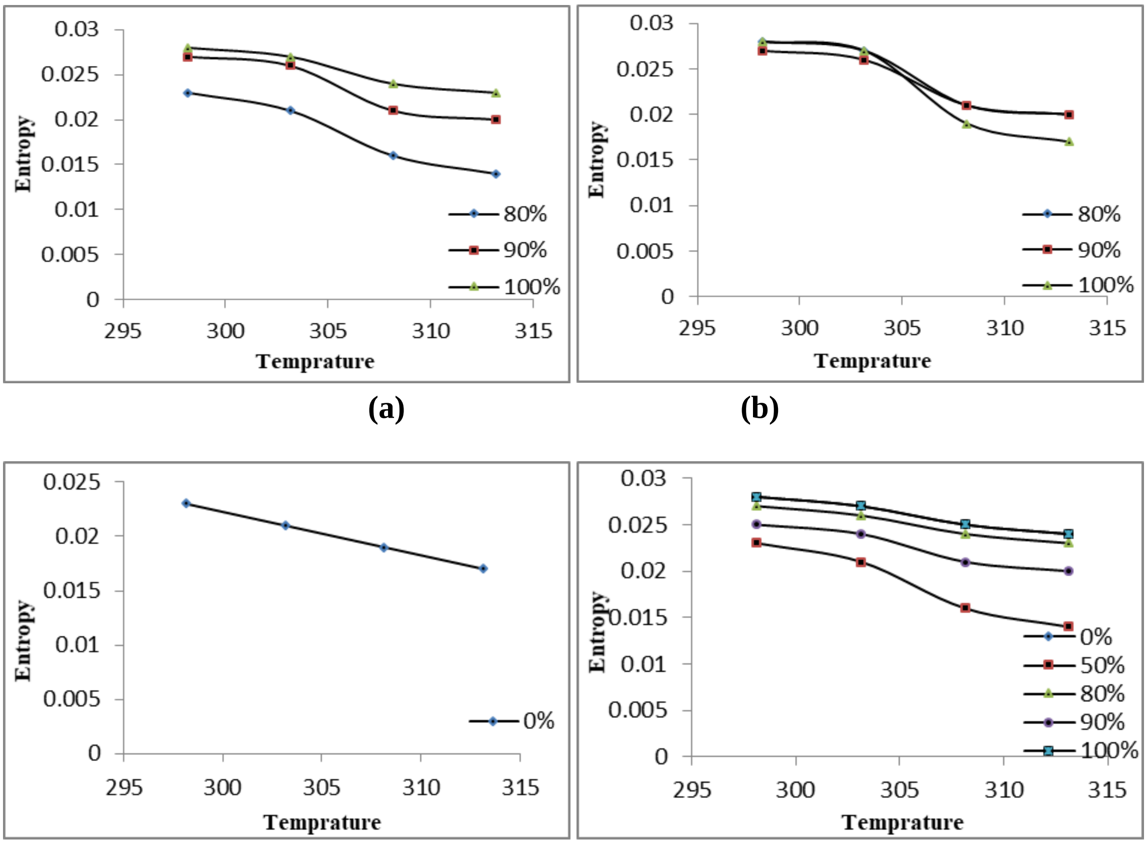


(c) **(d)**

Fig 7: Plots of Enthalpy of micellization vs. Temperature for (a) Sodium Stearate (b) Potassium Stearate (c) Sodium Oleate and (d) SLS in different alcohol-water systems system at various temperatures.

The results show that the ΔG°_{m} is negative. The negative value is in accordance with many workers. It can be generalized that the micellization process is exothermic at all temperature range studied. Again the negative value of ΔG°_{m} verifies the practicality of the process and the impulsive nature of adsorption. The negative value of ΔG°_{m} decrease with an increase in temperature indicates that the adsorption process becomes more encouraging at higher temperature [15]. The decreasing value of ΔG°_{m} with rising temperature also shows the tendency to drive equilibrium towards hydrophobic bonding.

Enthalpy is found to be negative and become further negative with increase of temperature. The negative enthalpy is associated by the way of disruption of the hydrophobic hydration surrounding the hydrophobic tail of the monomers. Again the enthalpy ΔH°_{m} becomes more negative with increasing temperature indicating the increasing exothermic nature at micellization. Literature suggests that the enthalpy change during micellization is a combined effect of the changes in enthalpy that arose from hydrophobic interactions, electrostatic interactions, hydration of polar group, and counter ion binding to the micelles [16, 17, 18].



(a) **(b)**

(c) **(d)**

Fig 8: Plots of Entropy of micellization vs. Temperature for (a) Sodium Stearate (b) Potassium Stearate (c) Sodium Oleate and (d) SLS in different alcohol system at various temperatures.

In the table 2 to 5, the positive values of entropy (ΔS˚m) are supposed to be due to the transfer of hydrophobic group of surfactants to micelle core in alcoholic and aqueous phase. This transfer has a strong effect on the hydrophobic hydration phenomenon, making it different from the usual solvent-solute interaction. The enhanced hydrogen bonding between water molecules in the neighbourhood leads to the tightening of water structure around hydrophobic group. Hydrophobic hydration causes internal torsion variation of chain to be classified in the solutions. Both of above mentioned factors lead to the decrease in entropy of system [19].

Table 2: Thermodynamic parameters (Gibbs free energy, Enthalpy, Entropy) for Sodium Oleate in alcohol-water solvent systems at different temperatures.

Solvent system	**Temperature (K)**	**ΔG˚m (KJ/mol)**	**ΔH˚$_m$ (KJ/mol)**	**ΔS˚$_m$ (KJ/mol)**
0%alcohol	298.15	-10.250	-3.251	0.023
	303.15	-9.859	-3.361	0.021
	308.15	-9.778	-3.789	0.019
	313.15	-9.309	-3.913	0.017

Table 3: Thermodynamic parameters (Gibbs free energy, Enthalpy, Entropy) for Sodium Stearate in alcohol-water solvent systems at different temperatures.

Solvent system	Temperature (K)	$\Delta G^{\circ}m$ (KJ/mol)	ΔH°_{m} (KJ/mol)	ΔS°_{m} (KJ/mol)
80%alcohol	298.15	-9.958	-2.958	0.023
	303.15	-9.619	-3.056	0.021
	308.15	-9.450	-4.324	0.016
	313.15	-8.881	-4.484	0.014
90%alcohol	298.15	-9.697	-1.418	0.027
	303.15	-9.619	-1.466	0.026
	308.15	-9.160	-2.589	0.021
	313.15	-8.881	-2.608	0.020
100%alcohol	298.15	-9.958	-1.552	0.028
	303.15	-9.859	-1.604	0.027
	308.15	-9.450	-1.784	0.024
	313.15	-9.309	-1.842	0.023

Table 4: Thermodynamic parameters (Gibbs free energy, Enthalpy, Entropy) for Potassium Stearate in alcohol-water solvent systems at different temperatures.

Solvent system	Temperature (K)	$\Delta G^{\circ}m$ (KJ/mol)	ΔH°_{m} (KJ/mol)	ΔS°_{m} (KJ/mol)
80%alcohol	298.15	-9.958	-1.552	0.028
	303.15	-9.859	-1.604	0.027
	308.15	-9.160	-2.589	0.021
	313.15	-8.881	-2.608	0.020
90%alcohol	298.15	-9.697	-1.418	0.027
	303.15	-9.619	-1.466	0.026
	308.15	-9.160	-2.589	0.021
	313.15	-8.881	-2.608	0.020
100%alcohol	298.15	-9.958	-1.552	0.028
	303.15	-9.859	-1.604	0.027
	308.15	-9.778	-3.789	0.019
	313.15	-9.309	-3.913	0.018

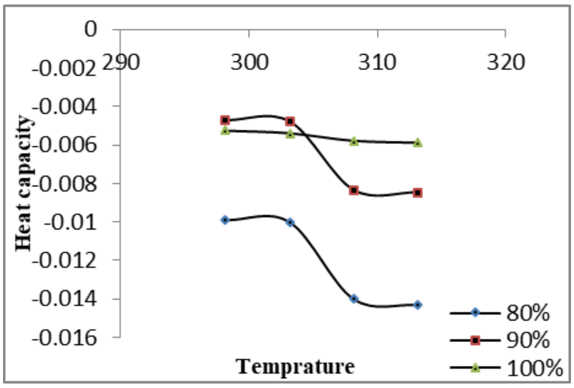
Table 5: Thermodynamic parameters (Gibbs free energy, Enthalpy, Entropy) for Sodium Laulryl Sulphate in alcohol-water solvent systems at different temperatures.

Solvent system	Temperature (K)	ΔG°_{m} (KJ/mol)	ΔH°_{m} (KJ/mol)	ΔS°_{m} (KJ/mol)
0%alcohol	298.15	-10.250	-1.699	0.028
	303.15	-10.125	-1.757	0.027
	308.15	-9.778	-1.973	0.025
	313.15	-9.604	-2.038	0.024
50%alcohol	298.15	-10.250	-3.251	0.023
	303.15	-9.859	-3.361	0.021
	308.15	-9.450	-4.342	0.016
	313.15	-8.881	-4.484	0.014
80%alcohol	298.15	-9.697	-1.418	0.027

	303.15	-9.619	-1.466	0.026
	308.15	-9.450	-1.784	0.024
	313.15	-9.309	-1.842	0.023
90%alcohol	298.15	-9.460	-1.847	0.025
	303.15	-9.297	-1.910	0.024
	308.15	-9.160	-2.589	0.021
	313.15	-8.881	-2.608	0.020
100%alcohol	298.15	-9.958	-1.552	0.028
	303.15	-9.859	-1.604	0.027
	308.15	-9.778	-1.973	0.025
	313.15	-9.604	-2.038	0.024

Table 6: Heat capacity values (J/mol) at CMCs for Sodium Stearate(SS), Potassium Stearate(PS), Sodium Oleate(SO) and Sodium Laulryl Sulphate(SLS) in alcohol-water systems at different temperatures.

System	**Temperature (K)**	**0% alcohol**	**50% alcohol**	**80% alcohol**	**90% alcohol**	**100% alcohol**
SDS	298.15	-0.00562	-0.0109	-0.00472	-0.00611	-0.00523
	303.15	-0.00575	-0.0110	-0.00484	-0.00634	-0.00536
	308.15	-0.00643	-0.0140	-0.00571	-0.00839	-0.00643
	313.15	-0.00658	-0.0143	-0.00589	-0.00850	-0.00657
Sodium stearate	298.15	-----	-----	-0.00990	-0.00471	-0.00526
	303.15	-----	-----	-0.01001	-0.00477	-0.00539
	308.15	-----	-----	-0.01401	-0.00833	-0.00578
	313.15	-----	-----	-0.01432	-0.00846	-0.00588
Potassium sterate	298.15	-----	-----	-0.00524	-0.00475	-0.00526
	303.15	-----	-----	-0.00535	-0.00484	-0.00539
	308.15	-----	-----	-0.00844	-0.00836	-0.01223
	313.15	-----	-----	-0.00856	-0.00847	-0.01243
Sodium oleate	298.15	-0.01099	-----	-----	-----	-----
	303.15	-0.01101	-----	-----	-----	-----
	308.15	-0.01222	-----	-----	-----	-----
	313.15	-0.01249	-----	-----	-----	-----



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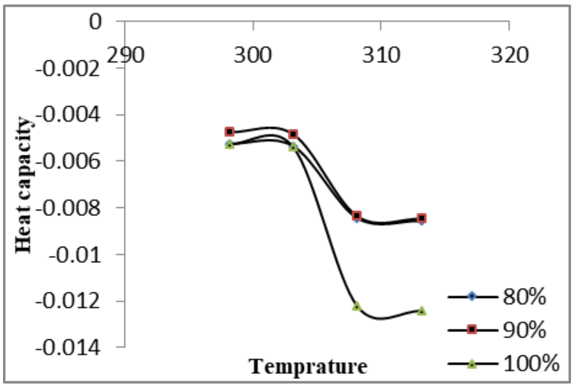

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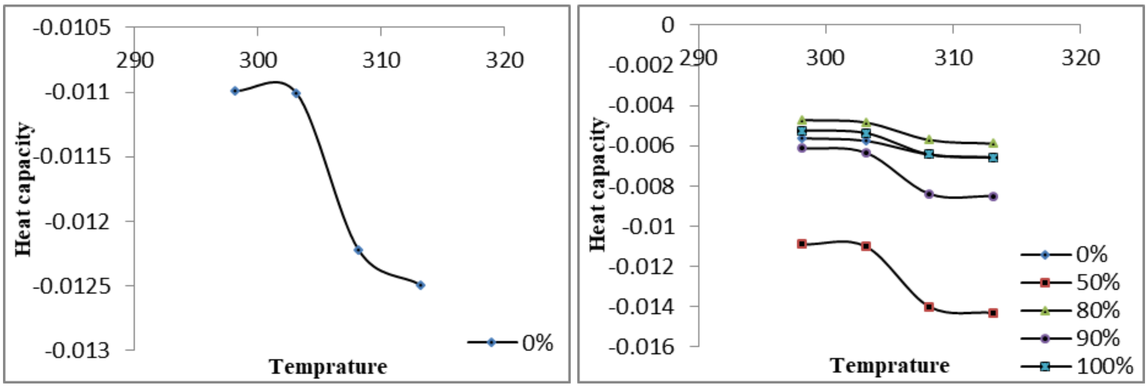

(c) (d)

Fig 9: Plots of Heat capacity vs. Temperature for (a) Sodium Stearate (b) Potassium Stearate (c) Sodium Oleate and (d) SLS in different alcohol water-systems at various temperatures

Heat capacity is very important to design various reaction and calculation in industrial field. Here the heat capacities at critical micelle concentration for the salts under study have been given in the table 6. The plots of heat capacity at CMCs vs. temperature are usually “S” shaped showing peculiar change in ΔC_p at CMCs with increasing temperature. On the average the heat capacities from 298.15 to 303.15K are seen to remain constant, but after 303K up to 308K it falls sharply. The reason for this falling may be due to the removal of solvent molecular from micelle or dissolvable of micelle in addition to increase of kinetic energy of all the molecules of the solution. Hydrogen bonding of solvent system may also get ruptured. But after 308K again the curves ΔC_p at CMC vs. temperature become horizontal to the axis, showing complete removal of solvent molecules attached to the micelles [20].

CONCLUSIONS

The present study describes the thermodynamic properties investigation through conductivity measurements through interaction that occurred between the selective anionic surfactants (Sodium Stearate(SS), Potassium Stearate(PS), Sodium Oleate(SO) and Sodium Laulryl Sulphate(SLS)). The outcomes from the experimental data uncover that the CMCs of these surfactants in the alcohol-water solvent systems increase with increasing temperatures. The various thermodynamic parameters, for example, Gibbs free energy (ΔG°_{m}), enthalpy (ΔH°_{m}), entropy (ΔS°_{m}), and heat capacity (ΔC_p) of the micelle formation are calculated from the conductivity data obtained. The values of the adjustment in Gibbs free energy and entropy showed that increase in temperature (298.15 to 313.15 K).The negative value of enthalpy indicates the exothermic micellization process and micellization becomes more exothermic with increasing temperature. The approaching out inclination for the hydrophobic part is in this reduced with the outcome that larger amount of surfactant molecule remains in the solution. Micelle formation would, therefore take place at higher surfactant concentration.

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