Thermodynamic study of anionic surfactant Sodium Dodecyl Sulphate by ultrasonic method

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Abstract

Surfactants are larger volume chemicals used in detergents, household cleaning and personal care products and to lesser extent in pesticides, herbicides, paints and plastics. Sodium dodecyl sulphate selected for the present study is an anionic surfactant whose head group is having a negative charge. It is highly effective surfactant and is used in any task requiring the removal of oily stains and residues. Ultrasonic velocity measurements of SDS have been carried out at different temperatures (308°K to 323°K) to determine the CMC, soap-solvent interaction and various thermodynamical parameters. The density and viscosity of aqueous solution of SDS from 2mM to 14mM concentration are measured using 10 ml specific gravity bottle and Ostwald viscometer. Thermodynamic parameters such as adiabatic compressibility, Rao's constant, Wada's constant, van der Waal's constant, internal pressure, free volume, molar cohesive energy and Gibb's free energy were computed. The internal pressure variation in aqueous solution of SDS is sensitive in ultrasonic parameters of molecular interactions either due to temperature variation or due to concentration variations. Various molecular interactions in these solutions have been analyzed on the basis of variation of above parameters and eventually emphasizing the possible molecular interactions in terms of structure making and structure breaking effects of SDS in water. The results show that the aqueous solution of SDS behaves like an ionic substance and acts as a structure maker at lower temperatures and becomes a structure breaker at higher temperatures. The critical micellar concentration (CMC) of SDS is estimated to be 10mM. SDS can be interpreted as an effective stain remover at higher temperatures and above CMC.

Keywords

Thermodynamic parameters, CMC, anionic surfactant, internal pressure, free volume.

Introduction

Surfactant is an abbreviation for surface active agents, which literally means active at a surface[1]. Surfactants are the single most important ingredients in laundry and household cleaning products, comprising from 15% to 40% of the total detergent formulation[2]. Surfactants contain two distinct grouping in their structure, polar or charged group at one end of it is the "head group" which is hydrophilic in nature and long chain of alkyl or aryl group is the "tail group" which is hyrophopic in nature. When surfactants are added to water at low concentration they are dispersed as discrete molecules. However at a particular concentration, surfactant molecules get associated to form aggregates or micelles[3-5]. This concentration is known as critical micellar concentration (CMC) which is an important property of surfactant. Above CMC, the surfactants exist as aggregates or micelles.

Anionic surfactants are usually chosen for surfactant based remediation procedures because of their lower degree of adsorption on soil than that by cationic and non-ionic surfactants[6]. Anionic surfactant sodium dodecyl sulphate ($(CH_3(CH_2)_{11}OSO_3Na)$) used has good detergent action because of its wetting power and high emulsification efficiency. Literature survey has revealed that SDS which is used as foaming agent in toothpaste may decrease the effectiveness of fluoride to preventing dental cavities.

The ultrasonic velocity technique has been used for studying solute-solvent interactions in a number of systems including organic liquids[7] and it is also used to determine the nature of molecular interactions in the systems. Here CMC of SDS is evaluated by ultrasonic method.

Experimental Study

Aqueous solutions of Sodium Dodecyl Sulphate of different concentrations were prepared with Analar grade salt and triple distilled water. The ultrasonic velocities of the solutions were measured using an ultrasonic interferometer (Mittal F-81D) with a single crystal at a frequency of 2 MHz. The accuracy in the velocity measurement is ±0.5%. The densities of the solutions were measured using specific gravity bottles and a digital balance with an accuracy of 0.0001 kg/m^3. Viscometric studies were carried out by Ostwald viscometer for various concentrations. Throughout the experiment, the temperature was maintained using a constant temperature bath with could maintain upto ± 0.1°C.

Computational Method

The thermodynamical parameters like adiabatic compressibility, Rao's constant, Wada's constant, van der Waal's constant, internal pressure, free volume, molar cohesive energy and Gibb's free energy have been calculated using the following relationships,

Adiabatic compressibility, $\beta = (1/U^2\rho)$ Kg^{-1}ms^2
Rao's constant, $R = (M_{eff}/\rho)* (U)^{(1/3)}$
Wada's constant, $B = (M_{eff}/\rho)* (\beta)^{(-1/7)}$
Van der Waal's constant, $b = (M_{eff}/\rho)*[1-(RT/M_{eff}U^2) *\{[1+(M_{eff}U^2/3RT)]^{(1/2)}-1\}]$
Internal pressure, $\pi_i = bRT*[k\eta/U]^{(1/2)}*(\rho^{(2/3)}/ M_{eff}^{(7/6)})$ Pascal
Free volume, $V_f = [M_{eff}U/k\eta]^{(3/2)}$ m^3
Molar cohesive energy $= \pi_i * V_m$ litre/mole
Gibb's free energy $\Delta G = KT \ln(KT\tau/h)$ KJmol^{-1}

Where, U = ultrasonic velocity (m/s), ρ = density (Kg/m^3), η = viscosity (Nsm^{-2}), M_{eff} = effective molecular weight, b = packing factor, R = gas constant ($8.314*10^7$), T = temperature (Kelvin), k = temperature independent constant ($4.28*10^9$), K = Boltzmann's constant ($1.3806*10^{-23}$)

Results and Discussion

The ultrasonic velocity of sound waves in a medium is fundamentally related to the binding forces between the molecules. Ultrasonic velocity measurements have been employed extensively to detect and assess weak and strong molecular interactions in binary liquids, because mixed solvents find practical applications in many chemical and industrial processes[8]. The determination of CMC of SDS in water has been done using the ultrasonic velocity, viscosity and density measurements. The values of CMC determined at different temperatures are in fair agreement.

The ultrasonic velocity, adiabatic compressibility, Rao's constant, Wada's constant, van der Waal's constant, internal pressure, free volume, molar cohesive energy and Gibb's free energy of SDS at different concentrations (2mM to 14mM) and different temperatures (308°K to 323°K) are given in table-1.

TABLE - 1

Adiabatic compressibility, Rao's constant, Wada's constant, van der Waal's constant, Internal pressure, Free volume, Molar cohesive energy, Gibb's free energy and $\Delta\pi_i$ of SDS at different concentrations (2mM to 14mM) and different temperatures (308°K to 323°K)

Thermodynamical Parameters	Concentration mole	Temperature (Kelvin)			
		308°K	313°K	318°K	323°K
Adiabatic Compressibility (10^{-10}Kg^{-1}ms^2)	0	4.4003	4.3552	4.3116	4.3054
	0.002	4.3558	4.3212	4.3018	4.2875
	0.004	4.3095	4.3073	4.2734	4.2590
	0.006	4.2789	4.2666	4.2266	4.2103
	0.008	4.2565	4.2322	4.1891	4.1846
	0.010	4.3595	4.2932	4.2828	4.2487
	0.012	4.2751	4.1862	4.1793	4.1278

	0.014	4.2275	4.2182	4.1827	4.1066
Rao’s Constant	0	965.52	969.25	973.15	975.89
	0.002	968.14	972.28	973.84	976.53
	0.004	970.18	971.46	973.86	976.48
	0.006	969.72	972.83	975.46	977.59
	0.008	971.06	973.17	976.14	978.03
	0.010	971.08	974.03	975.22	977.50
	0.012	970.46	976.52	977.86	980.98
	0.014	974.86	977.44	980.95	984.67
Wada’s Constant	0	546.69	548.50	550.40	551.72
	0.002	548.01	550.01	550.77	552.08
	0.004	549.04	549.66	550.83	552.09
	0.006	548.86	550.37	551.65	552.67
	0.008	549.55	550.58	552.02	552.94
	0.010	549.61	551.04	551.61	552.72
	0.012	549.35	552.29	552.94	554.45
	0.014	551.53	552.78	554.48	556.28
Van der Waal’s Constant	0	16.4084	16.4365	16.4675	16.4976
	0.002	16.4298	16.4682	16.4749	16.5006
	0.004	16.4414	16.4512	16.4638	16.4884
	0.006	16.4222	16.4549	16.4681	16.4843
	0.008	16.4335	16.4460	16.4625	16.4806
	0.010	16.4809	16.4875	16.4923	16.5030
	0.012	16.4355	16.4777	16.4864	16.5010
	0.014	16.4936	16.5074	16.5353	16.5474
Internal Pressure (10^{12} Pascal)	0	7.8915	7.6075	7.3525	7.1362
	0.002	7.8677	7.5359	7.2230	7.2274
	0.004	7.8941	7.6288	7.2295	7.2287
	0.006	7.8751	7.8174	7.0899	7.1136
	0.008	8.0139	7.5293	7.1759	6.7754
	0.010	8.0492	7.3755	7.1133	6.8170
	0.012	8.1659	7.4840	7.1809	6.7986
	0.014	7.8414	7.1794	7.1308	6.7615
Free Volume (10^{-3} m^3)	0	0.8321	0.9712	1.1237	1.2822
	0.002	0.8381	0.9959	1.1843	1.2342
	0.004	0.8291	0.9621	1.1831	1.2358
	0.006	0.8374	0.8942	1.2547	1.2983
	0.008	0.7938	1.0024	1.2116	1.5037
	0.010	0.7779	1.0603	1.2378	1.4712
	0.012	0.7499	1.0176	1.2058	1.4861
	0.014	0.8429	1.1481	1.2243	1.5030
Molar Cohesive Energy (10^{11}litre/mole)	0	1.4302	1.3813	1.3376	1.3178
	0.002	1.4272	1.3705	1.3146	1.3178
	0.004	1.4325	1.3858	1.3147	1.3169
	0.006	1.4272	1.4200	1.2891	1.2951
	0.008	1.4531	1.3666	1.3040	1.2331
	0.010	1.4646	1.3426	1.2957	1.2428
	0.012	1.4810	1.3605	1.3066	1.2381

	0.014	1.4255	1.3077	1.3013	1.2341
Gibb’s free energy (10^{-20}KJmol^{-1})	0	3.361	3.315	3.272	3.235
	0.002	3.357	3.307	3.257	3.245
	0.004	3.358	3.316	3.256	3.243
	0.006	3.353	3.335	3.237	3.227
	0.008	3.368	3.300	3.245	3.184
	0.010	3.379	3.288	3.244	3.194
	0.012	3.385	3.294	3.246	3.184
	0.014	3.350	3.262	3.243	3.181
$\Delta\pi_i$	0.002	-2.37	-7.16	-12.94	9.100
	0.004	0.25	2.12	-12.29	9.233
	0.006	-1.64	20.99	-26.26	-2.276
	0.008	12.24	-7.82	-17.66	-36.09
	0.010	15.76	-23.19	-23.92	-31.93
	0.012	27.43	-12.35	-17.15	-33.77
	0.014	-5.00	-42.80	-22.16	-37.49

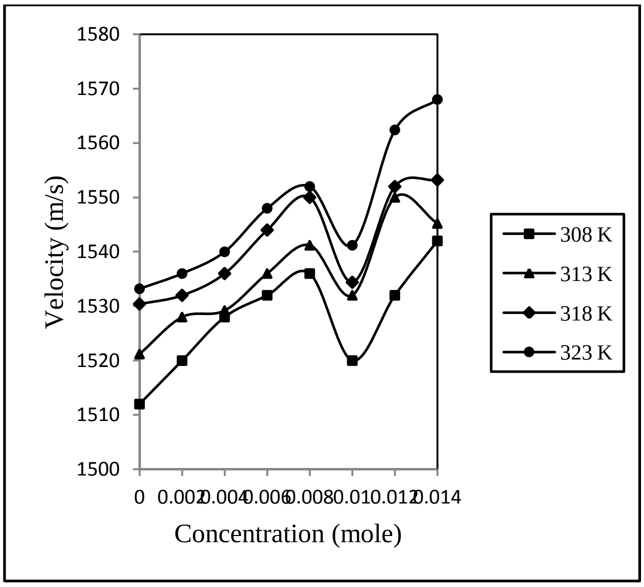

Figure: 1 Velocity Vs Concentration of SDS

From the value of velocity and its plot against concentration(figure-1), it is clear that the ultrasonic velocity initially increases and suddenly acquires a minimum value (10mM) and then continues to increase with increasing concentration of surfactant. This concentration 10mM is the CMC of SDS. At CMC aggregation of monomers to form aggregates known as micelles takes place hence at CMC, ultrasonic velocity is found be minimum. This observation suggests that the ultrasonic velocity measurement can be relied upon to yield meaningful information about the micelle aggregation in aqueous solution. The CMC value of SDS is found to be 10mM at 308°K which is close to the already reported literature value 8.10mM at 303°K [9].

The nature of adiabatic compressibility is found to be in reverse trend to that of ultrasonic velocity variation shown in figure-2.

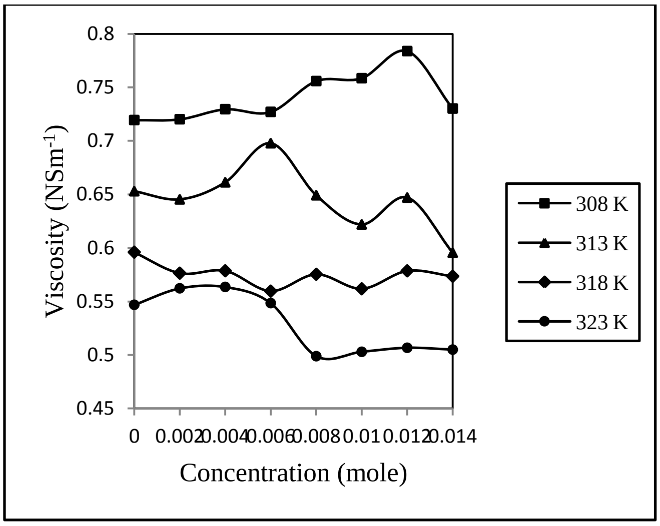

Figure: 2 Viscosity Vs Concentration of SDS

Compressibility measurements are highly accurate and yield interesting information about the molecular interactions in solutions. It is the fractional decrease of volume per unit increase of pressure when no heat flows in or out. When the solute is dissolved in solvent, due to the influence of electrostatic field the water structure tends to break and the solute surrounded water molecules are more compactly packed, hence compressibility decreases with increasing concentration[10] shown in (figure-3).

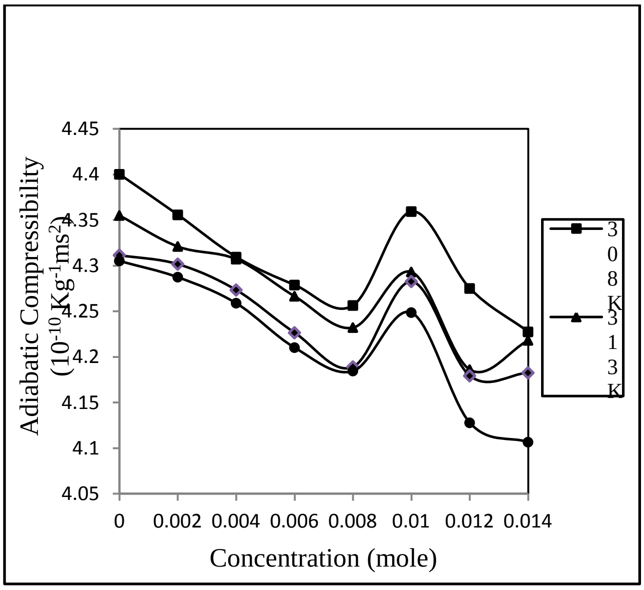

Figure: 3 Adiabatic Compressibility Vs Concentration of SDS

Van der Waal's constant shows the similar trend as velocity and follows reverse trend as that of adiabatic compressibility (figure-4).

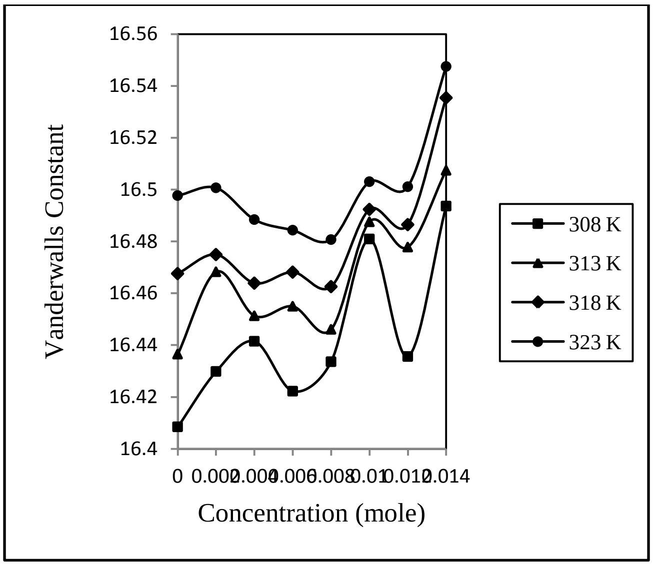

Figure: 4 Van der Waal's Constant Vs Concentration of SDS

The nonlinear variation in viscosity of solution with concentration of solute was qualitatively described to hydrogen bonding and their result confirms that the sign and magnitude of such deviation depends on the strength of interaction between unlike molecules. These nonlinear variations of viscosity at higher temperatures indicate that SDS effectively removes the stain from clothes at these temperatures which is represented by calculated parameter values. The value of Rao's constant and Wada's constant shows non linear variation with the increase of concentration. They are represented in figures 5 and 6 which are inversely resembles the viscosity nature.

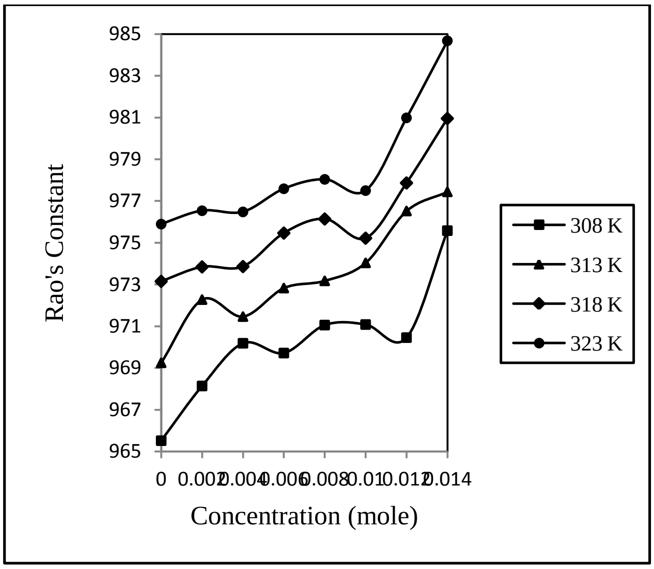

Figure: 5 Rao's Constant Vs Concentration of SDS

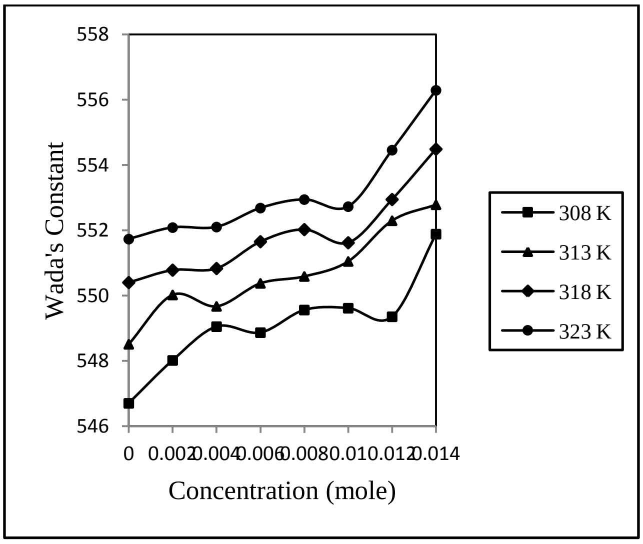

Figure: 6 Wada's Constant Vs Concentration of SDS

The measurement of internal pressure is important in the study of thermodynamical properties of liquids. It is the cohesive force which is the resultant of force of attraction and force of repulsion between the molecules[11-12]. As the repulsive forces become prominent showing relatively lower values of internal pressure. But at a concentration 0.012 mole, the values of internal pressure are relatively higher predicting greater force of attraction between the hydrophilic part of surfactant and water molecules. The internal pressure is found to decrease with rise in temperature, because when the temperature is increased there is a tendency for interaction which may further reduce the cohesive forces and ultimately leads to decrease in internal pressure (figure-7). Similar measurement has been done for SDS with formamide as solvent by earlier workers[13]. The variation in internal pressure and free volume resembles the same as in the case of water solvent.

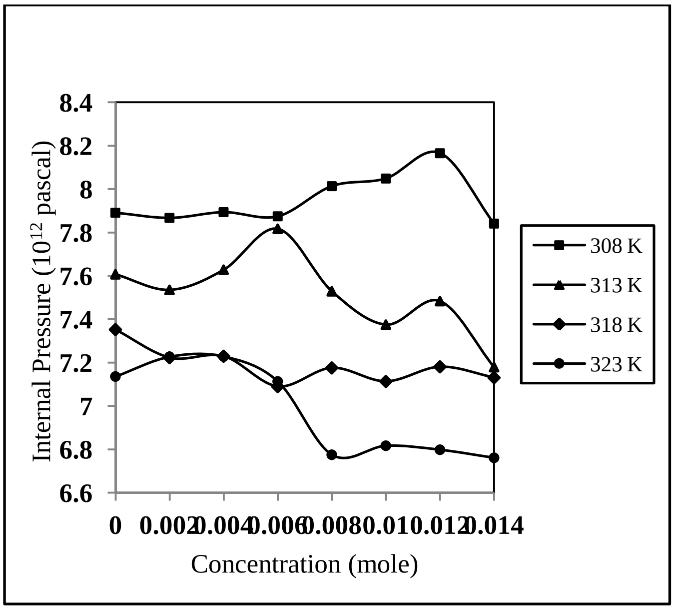

Figure: 7 Internal Pressure Vs Concentration of SDS

Free volume is one of the significant factors in explaining the variations in the physio-chemical properties of liquids [14]. The exactly reverse trend of internal pressure was observed in the case of free volume (figure-8).The weakening of molecular association leads to a larger free volume available for molecular motion and the reverse effect give rise to smaller free volume. Molar Cohesive energy (figure-9) and Gibb's free energy (figure-10) shows similar variation as that of internal pressure. This may be due to molecular interaction between solute-solvent molecules increases with the addition of surfactant which is confirmed by the previous parameters also.

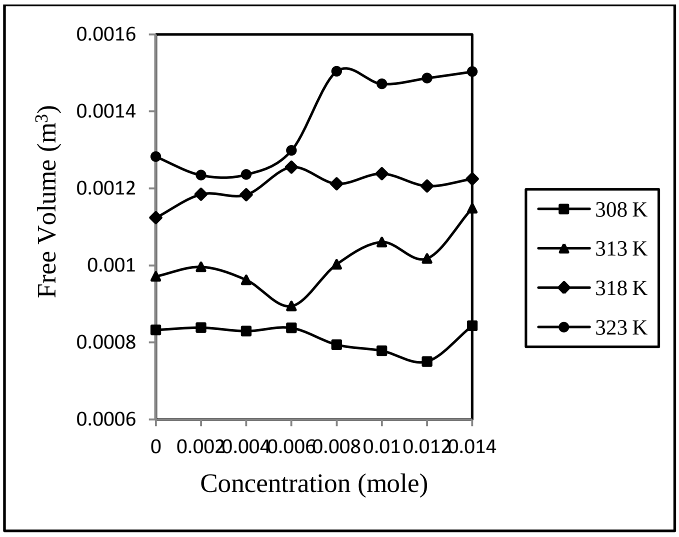

Figure: 8 Free volume Vs Concentration of SDS

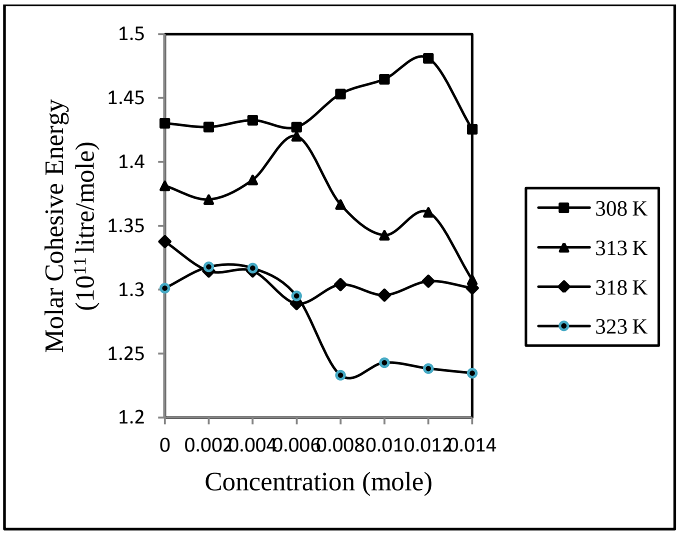

Figure: 9 Molar Cohesive Energy Vs Concentration of SDS

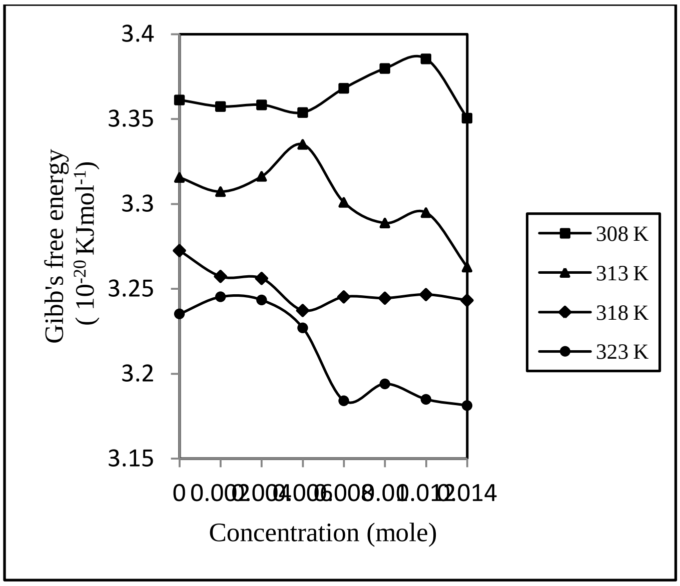

Figure: 10 Gibb's free energy Vs Concentration of SDS

The variation of internal pressure with concentration have been treated quantitatively by some researchers and found that it is a quadratic function of concentrations [15]. They formulated the equation, $\pi_s = \pi_i + Am^2 + Bm$ where, π_i is the internal pressure of solvent, π_s is the internal pressure of solution, m is the concentration, A and B are temperature dependent constants. This is found to be true in many cases of electrolytes, the same was observed in SDS.

The difference $\Delta\pi_i$ between π_i and π_s predicts the nature of solute. If $\Delta\pi_i$ is positive, the solute has the tendency to enhance the internal pressure of the solvent when added to it and if it is negative the internal pressure value will decrease, which is cohesive forces gets loosened with the addition of solute. The variation of $\Delta\pi i$ values with concentration shown in (figure-11).

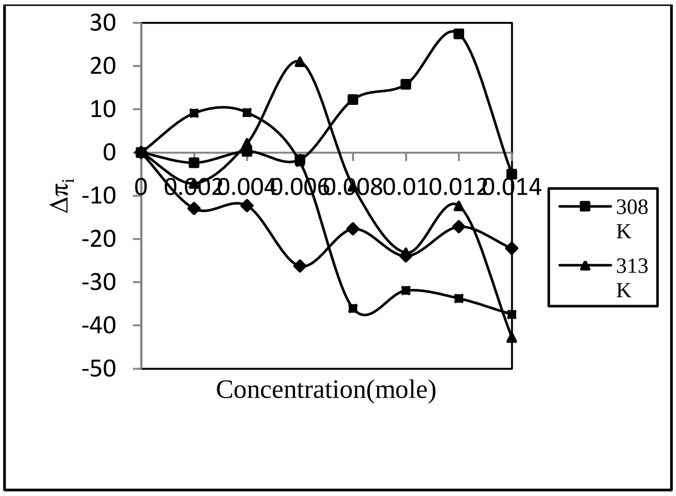

Figure: 11 $\Delta\pi_i$ Vs Concentration of SDS

In the case of SDS the $\Delta\pi_i$ value is found to be positive at low temperatures and changes it value to negative at higher temperatures. The change in $\Delta\pi_i$ leads to the conclusion that SDS acts as a structure maker at the lower temperatures and becomes a structure breaker at higher temperatures.

Conclusion

Ultrasonic velocity, density and viscosity studies are employed in the anionic surfactant SDS. The resultant values of thermodynamical parameters suggest that SDS as an effective stain remover at higher temperatures and above CMC. Hence, it finds its usage in the laundry and household purposes.

Acknowledgement

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