

# Acoustic and Thermodynamic properties of sodium silicate in aqueous Ammonium Lauryl Sulphate by ultrasonic studies

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## Abstract

Anionic surfactant plays a major role in cleaning product due to their superior detergency performance. The primary function of a builder is to reduce water hardness and hold the cleaning behaviour of the surfactants. Thus, builder is to enhance the surfactant to upgrade their cleaning action, bonding with metal ions and helping to remove and disperse particulate soils. The ultrasonic study of sodium silicate (builder) in aqueous Ammonium Lauryl Sulphate (ALS - anionic surfactant) is investigated. The density ( $\rho$ ), viscosity ( $\eta$ ) and ultrasonic velocity ( $U$ ) of sodium silicate in different concentrations of aqueous ALS solutions (4mM, 5mM & 7mM) are measured at distinctive temperatures (303K, 308K and 313K). The acoustic and thermodynamic parameters such as specific acoustic impedance ( $Z$ ), intermolecular free length ( $L_f$ ), surface tension ( $\sigma$ ), internal pressure ( $\pi_i$ ), free volume ( $V_f$ ) and change in internal pressure ( $\Delta\pi_i$ ) are calculated. The qualitative correlation between internal pressure and free volume with concentration is also evaluated.

**Keywords:** *specific acoustic impedance, intermolecular free length, surface tension, internal pressure and free volume*

## 1. Introduction

The ultrasonic studies are extensively used to estimate the acoustic and thermodynamic behaviour of liquids or solutions and predict the intermolecular interactions existing in them. It furnishes available information about the state of liquids and explains many physical properties of liquids. Ultrasonic research in solution have made possible not only for the valuation of physico chemical properties of the solutes but also more

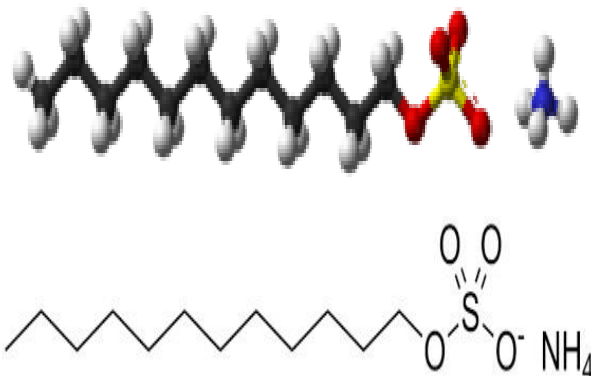
reliability on the interpretation of inter and intra molecular interactions, the nature and the strength of the solutions (Baldev Raj, V. et.al, 2004) <sup>[1]</sup>.

The need for efficient cleaning and washing of different types of fabrics has led to an ongoing research which has forced the researchers and scientists to develop a new era of detergents which not only have an enhanced cleaning action, but also are bio-degradable to an excellent quality (Anu Keshwani et.al, 2015)<sup>[2]</sup>. A number of researchers <sup>[3-7]</sup> have investigated the molecular interactions of surfactants solutions. A detergent can be a water-soluble cleaning agent which combines with impurities and dirt on the fabric and makes them more soluble in water. Detergent chemically is a surfactant or a mixture of surfactants that are more soluble in hard water (Ainsworth, S. J., 1994) <sup>[8]</sup>. Surfactants are “Surface active cleaning agent” that are compounds that cover the surface tension between two liquids. Surfactant contains both polar or hydrophilic (hydro-water, philic -friendship) head group and non-polar or hydrophobic (hydro-water, phobic-fear) tail end. Surfactants are classified by dependent on the molecular composition and the nature of dissociation of their polar head groups.

Anionic surfactants work best because of their excellent foam and lather characteristics, are typically used as primary surfactants to remove dirt, clay and some oily stains. These surfactants work fully ionization when added to water and have a negative charge. The negatively charged surfactants bind to the positively charged particles like soil and clay.

Anionic surfactants are effective in removing particulate soils (Jesse J. Williams, 2007) <sup>[9]</sup>. They tend to be affected by water hardness ions and

generate higher foam levels than other surfactant classes. ALS surfactant lowers the surface tension of water, making the water spread more easily. In ALS, where  $SO_4$  end is the anion (in aqueous solution dissociated), ammonium ion is its counter ion and the long chain of carbon and hydrogen is its hydrophobic tail end (Carel J. Vanoss, 2008) <sup>[10]</sup>. ALS is added to product as foaming agent and as a detergent. It can be also used in hard water. The builder in detergent formulation is the second most important aspects. A builder at lower concentration enhances the effect of the surfactants by deactivating calcium and magnesium ions present in water (Rutkowski, B.J., 1981) <sup>[11]</sup>. Builders are thus called as water softeners which work by complexing or precipitating or ion-exchange mechanism (Krischner E. M., 1998) <sup>[12]</sup>. The present investigation is to elucidate the effect of builder sodium silicate in aqueous anionic ALS surfactant at different concentrations and temperatures, which will be helpful to reinforce the knowledge for further study. The acoustic and thermodynamic study of the surfactant systems are of great importance in theoretical and practical aspects.



**Fig 1 Molecular structure of Ammonium Lauryl Sulfate**

Sodium silicate serves as a builder. It can modify the adsorption of the detergent on the surface and/or soil and also act as suspending agent (Wells, A. F., 1984) <sup>[13]</sup>. Sodium silicate provides a safe level of alkalinity to ensure good cleaning. It is a common corrosion inhibitor. In detergency auxiliaries the detergent granules gain the ruggedness from the coating of silicates (Gerard Lagaly et.al, 2015) <sup>[14]</sup>.

## 2. Experimental techniques

Ammonium Lauryl Sulphate from Sigma Aldrich Chemicals, USA and sodium silicate from Lobal Chemie Pvt. Ltd., Mumbai were used for this study. Deionized water was used for the preparation of the solutions. Densities of the solution are measured by 10ml specific gravity bottle with an accuracy of  $\pm 0.1 \text{ Kg.m}^{-3}$ . The

required weighing was done on Denver digital balance with a precision of  $\pm 0.0001 \text{ g}$ . An Ostwald's viscometer (10ml capacity) was used for the viscosity measurement and the time flow of the solution is measured using a Racer stop watch with the accuracy of  $\pm 0.01 \text{ s}$ . The ultrasonic velocities of solutions are measured by using Ultrasonic interferometer (Model F-81, Mittal Enterprises, New Delhi) with an accuracy of  $\pm 0.5\%$ . The desired temperature was maintained constant by an electronic digital constant temperature bath (Raaga Industries, Chennai). The accuracy of the temperature measurement is  $\pm 0.1^\circ \text{C}$ .

## 3. Formulation

The acoustic and thermodynamic parameters were computed from the measured data using the following relations (1-5).

Specific acoustic impedance:

$$Z = \rho \cdot U \quad (1)$$

Intermolecular free length:

$$L_f = K \cdot \beta^{\frac{1}{2}} \quad (2)$$

Internal pressure:

$$\pi_i = bRT \left[ \frac{k \cdot \eta}{U} \right]^{\frac{1}{2}} \cdot \frac{\rho^{\frac{3}{2}}}{M^{\frac{3}{2}}} \quad (3)$$

Free volume:

$$V_f = \left[ \frac{U \cdot M_{\text{eff}}}{\eta \cdot k} \right]^{\frac{3}{2}} \quad (4)$$

Surface tension:

$$\sigma = U^{\frac{3}{2}} * 6.3 * 10^{-4} * \rho \quad (5)$$

where, K is Jacobson's constant; b stands for cubic packing factor, R is a gas constant ( $8.314 \text{ K.J mol}^{-1}$ ); T is absolute temperature; k is temperature dependent constant ( $4.28 \times 10^9$ );  $M_{\text{eff}}$  is effective molecular weight of the solution.

## 4. Results and Discussions

The density ( $\rho$ ), viscosity ( $\eta$ ) and ultrasonic velocity (U) values of different molarities of sodium silicate (1mM-5mM) in three different concentrations (4mM, 5mM & 7mM) of aqueous ALS solution are measured experimentally at 303K, 308K and 313K temperatures and are given in table 1.

### Density ( $\rho$ ):

It is observed from table 1, that the density values increases with increase in concentration of sodium

silicate (1mM-5mM) in aqueous ALS solution due to the dissociation of sodium silicate into sodium ( $\text{Na}_2^+$ ) and silicate ( $\text{SiO}_3^-$ ) ions. These ions may interact with the hydrophobic and hydrophilic parts of ALS through hydrogen bonding. In other words, the addition of sodium silicate leads to shrinkage in volume of ALS due to absorption of solvent in dissolved solute. The decrease in density values with increase in ALS concentration and temperature indicates the decrease in cohesive force due to increase in thermal agitation in this solution. This results in volume expansion and thereby decreases the density of the solution (Thirumaran, S. et.al, 2011) <sup>[15]</sup>.

### Viscosity ( $\eta$ ):

Viscosity is a fundamental parameter to understand the structural and molecular interactions take place in the solution. Variation of viscosity is attributed to the change in structure. It is observed from the viscosity values that it increases with increasing molarity of sodium silicate and ALS concentration, whereas decrease with rise in temperature. At 313K, viscosity decreases for all the ALS concentrations which indicate if the temperature is increased, the cohesive forces get weaken and the molecules become more loosen, subsequently the solvent structure get broken (Sunanda S. Aswale et.al, 2012)<sup>[16]</sup>. The increase in viscosity with concentration implies that solute-solvent molecules are tightly bounded by attractive inter-molecular force which intern increases the binding energy between them.

### Ultrasonic velocity (U):

The increase in ultrasonic velocity with increase in concentration of sodium silicate at all temperatures may be confirmed that the entity of solute-solvent interaction due to the increase of greater cohesion which creates intermolecular forces (Chinmankar O.P et.al, 2011) <sup>[17]</sup>. In ALS solutions, the sulphate anions and the ammonium counter ion dissociated from each other are interacted with sodium ( $\text{Na}_2^+$ ) and silicate ( $\text{SiO}_3^-$ ) ions. The hydrophilic (polar) heads of sulphate portion towards the water phase and the non-polar hydrophobic tails pointing opposite to water phase. The water molecules around the polar heads which disrupts their ability of hydrogen bond formation with other nearby water molecules; this allows the solution for solvent-solvent interaction, which in turn create displacement of ions. The decrease of velocity with increase in the concentration of ALS may increases the micelles formation. This is because ALS reduces the repulsive forces between the head groups at the surface of the micelle, so it allows micelles formation. In ALS solution when the concentration of surfactant solution increases it is favorable for free molecules combine together to form micelles and the free surfactant molecules are

not held in a permanent place, there is an exchange of free molecules in the solution that establish an equilibrium between micelles and free molecules. With the addition of sodium silicate, the sodium ( $\text{Na}_2^+$ ) ion interacts with the hydrophilic sulfate ( $\text{SO}_4^-$ ) head group of ALS and silicate ( $\text{SiO}_3^-$ ) ions surrounded by hydrophobic tails which enhance the ALS molecules to the removal of stain. At CMC, the free molecules become constant which initiate the resist of forming micelles and have no space for interaction which tends to decreases the velocity (Katz, C.A. et.al, 2008) <sup>[18]</sup>.

### Specific acoustic impedance (Z):

Dispersion and appearance of the internal energy in the surfactant solution was determined by specific acoustic impedance. Specific acoustic impedance exhibits the same trend to that of ultrasonic velocity and inversely proportional to that of compressibility which indicates the hydrophobic interaction exists between ALS and sodium silicate. It is also noticed from table 2 that Z increases with increases in molarity of sodium silicate at all temperatures indicating strong molecular association between solute and solvent due to hydrogen bonding. The decrease of Z value with increase of ALS concentration is clearly shows that the velocity plays an important role. The concentration of ALS increases more accumulation of volume in the solution due to rise in temperature, size and shape enlargement of hydrophobic group. This shows that the micelles formations are well placed in the surfactant solution. The solvent molecules compared to the solute particles lead to dominant which indicates strong solute-solvent interaction. This confirms the decrease in Z (Anushri Gupta et.al, 2013) <sup>[19]</sup>.

### Intermolecular free length ( $L_f$ ):

According to Eyring and Kincaid, as the ultrasonic velocity increases, free length decreases with increase in concentration. The same results are found with the addition of sodium silicate in ALS is due to the strong intermolecular force between the solute-solvent molecules. When solute is added to the solvent, the intermolecular space available between them is decreased. This reduction of space causes volume elaboration of the solvent ALS. There is an increase in volume that causes an increase in  $L_f$ . This reveals that there is a strong solute-solvent interaction. But the ultrasonic velocity decreases with increasing ALS concentration and therefore  $L_f$  increases at all temperatures. The available free space is rises by the strength and size of hydrophobes of increased ALS. This suggests that  $L_f$  depends on the molecular packing and extent of molecular association in the solution (Ravichandran S., 2008) <sup>[20]</sup>.

**Table 1: Density ( $\rho$ ), viscosity ( $\eta$ ) and ultrasonic velocity (U) values of sodium silicate (1mM to 5mM) in three different concentrations of ALS at 303K, 308K and 313K**

Molarity M mol. l <sup>-1</sup>	$\rho$ (Kg.m <sup>-3</sup> )			$\eta$ (10 <sup>-3</sup> Nsm <sup>-2</sup> )			U (ms <sup>-1</sup> )		
	303K	308K	313K	303K	308K	313K	303K	308K	313K
<b>4mM ALS + sodium silicate</b>									
0	999.14	995.76	994.67	0.8222	0.7223	0.6739	1556	1560	1564
0.001	1001.15	999.14	997.34	0.8271	0.7272	0.6818	1562	1566	1572
0.002	1001.86	999.61	999.03	0.8312	0.7296	0.6857	1566	1570	1576
0.003	1002.02	1000.05	999.60	0.8341	0.7358	0.6899	1570	1576	1580
0.004	1002.49	1001.10	1000.58	0.8381	0.7395	0.6941	1574	1580	1584
0.005	1003.59	1001.84	1001.37	0.8423	0.7415	0.6971	1578	1584	1588
<b>5mM ALS + sodium silicate</b>									
0	998.75	995.33	994.20	0.8231	0.7313	0.6703	1538	1542	1552
0.001	1000.03	997.55	997.03	0.8291	0.7375	0.6770	1544	1548	1558
0.002	1000.45	999.06	998.77	0.8331	0.7389	0.6806	1548	1552	1562
0.003	1000.81	999.79	999.42	0.8362	0.7442	0.6848	1552	1556	1566
0.004	1001.24	1000.46	1000.44	0.8407	0.7482	0.6889	1556	1560	1570
0.005	1001.85	1001.06	1001.01	0.8451	0.7503	0.6920	1560	1564	1574
<b>7mM ALS + sodium silicate</b>									
0	996.36	995.27	993.82	0.8284	0.7357	0.6666	1524	1530	1536
0.001	997.85	996.48	996.28	0.8348	0.7426	0.6724	1528	1535	1542
0.002	999.09	997.89	997.38	0.8367	0.7458	0.6767	1532	1540	1546
0.003	999.71	998.34	997.89	0.8401	0.7506	0.6801	1536	1544	1550
0.004	1000.49	998.70	998.48	0.8444	0.7546	0.6836	1540	1548	1554
0.005	1001.02	999.49	999.29	0.8487	0.7569	0.6873	1544	1552	1558

**Table 2: Specific acoustic impedance (Z), intermolecular free length (L<sub>f</sub>) and surface tension ( $\sigma$ ) values of sodium silicate (1mM to 5mM) in three different concentration of ALS at 303K, 308K and 313K**

Molarity M	Z (10 <sup>6</sup> kgm <sup>-2</sup> s <sup>-1</sup> )			L <sub>f</sub> (10 <sup>-11</sup> m)			$\sigma$ (10 <sup>-3</sup> Nm <sup>-1</sup> )		
	303K	308K	313K	303K	308K	313K	303K	308K	313K
<b>Water + ALS 4mM + Sodium silicate</b>									
0	1.5547	1.5534	1.5557	4.0664	4.0933	4.1155	38.635	38.652	38.759
0.001	1.5638	1.5647	1.5678	4.0467	4.0707	4.0891	38.937	39.008	39.162
0.002	1.5689	1.5694	1.5745	4.0349	4.0594	4.0752	39.114	39.176	39.378
0.003	1.5732	1.5761	1.5794	4.0243	4.0430	4.0637	39.270	39.418	39.551
0.004	1.5779	1.5817	1.5849	4.0131	4.0307	4.0515	39.439	39.610	39.740
0.005	1.5837	1.5869	1.5902	4.0008	4.0190	4.0397	39.633	39.790	39.922
<b>Water + ALS 5mM + Sodium silicate</b>									
0	1.5361	1.5348	1.5430	4.1148	4.1420	4.1483	37.952	37.970	38.296
0.001	1.5440	1.5442	1.5534	4.0962	4.1213	4.1264	38.223	38.276	38.628
0.002	1.5487	1.5505	1.5600	4.0847	4.1076	4.1123	38.388	38.483	38.844
0.003	1.5533	1.5557	1.5651	4.0734	4.0955	4.1004	38.551	38.660	39.019
0.004	1.5579	1.5607	1.5707	4.0621	4.0837	4.0879	38.716	38.835	39.209
0.005	1.5629	1.5657	1.5756	4.0505	4.0720	4.0764	38.889	39.008	39.381
<b>Water + ALS 7mM + Sodium silicate</b>									
0	1.5184	1.5228	1.5265	4.1575	4.1746	4.1923	37.345	37.525	37.691
0.001	1.5247	1.5296	1.5363	4.1436	4.1585	4.1708	37.548	37.755	38.006
0.002	1.5306	1.5367	1.5420	4.1302	4.1420	4.1577	37.743	37.993	38.196
0.003	1.5356	1.5414	1.5467	4.1181	4.1304	4.1459	37.914	38.158	38.364
0.004	1.5408	1.5460	1.5516	4.1058	4.1190	4.1340	38.092	38.321	38.535
0.005	1.5456	1.5512	1.5569	4.0941	4.1067	4.1218	38.261	38.499	38.715

### Surface tension ( $\sigma$ ):

Surface tension is caused by the attraction between the molecules of liquid by intermolecular forces at the interface (Adamson A.W., 1997) [21]. It is seen from table 2 that the surface tension increases with increase in molarity of sodium silicate and temperature. The increase in surface tension indicates the increasing enhancement of ALS with the addition of sodium silicate. Surface tension depends on the nature of solute-solvent interaction, surrounding environment and temperature. The increased values increases the cohesive force due to thermal energy and the intermolecular forces between water molecules and hydrophilic group of ALS. On the other hand, the addition of ALS forms a number of micelles which alters the structure of

water by breaking the hydrogen bond and interacts with sodium silicate ions. The influence of the surrounding hydrophobes interacts with solute molecules are due to the adhesive force acting at the interface. This creates a mono molecular layer (free molecules) on the interface that reduces the surface tension (Salager J, 2002) [22]. The surface tension values for 7mM ALS is minimum. This shows that stain removal is greater in 7mM ALS than in other solutions.

**Table 3: Internal pressure ( $\pi_i$ ), free volume ( $V_f$ ), Change in internal pressure( $\Delta\pi_i$ ) values of sodium silicate (1mM to 5mM) in three different concentration of ALS at 303K, 308K and 313K**

Molarity M	$\pi_i$ ( $10^8 \text{ Nm}^{-2}$ )			$V_f$ ( $10^{-8} \text{ m}^3 \text{ mol}^{-1}$ )			$\Delta\pi_i$		
	303K	308K	313K	303K	308K	313K	303K	308K	313K
<b>Water + ALS 4mM + sodium silicate</b>									
0	25.6241	24.3271	23.8314	2.2863	2.7874	3.1050	-	-	-
0.001	25.6772	24.4099	23.9446	2.2801	2.7764	3.0758	0.0530	0.0829	0.1132
0.002	25.7122	24.4192	24.0024	2.2728	2.7744	3.0625	0.0881	0.0921	0.1710
0.003	25.7190	24.4758	24.0471	2.2706	2.7562	3.0473	0.0949	0.1487	0.2157
0.004	25.7480	24.5157	24.0981	2.2638	2.7470	3.0324	0.1239	0.1886	0.2666
0.005	25.7907	24.5224	24.1249	2.2564	2.7474	3.0254	0.1665	0.1953	0.2934
<b>Water + ALS 5mM + sodium silicate</b>									
0	25.6975	24.5338	23.7744	2.2525	2.7002	3.1070	-	-	-
0.001	25.7549	24.6187	23.8848	2.2420	2.6828	3.0800	0.0574	0.0849	0.1104
0.002	25.7829	24.6277	23.9381	2.2354	2.6866	3.0685	0.0854	0.0939	0.1636
0.003	25.7959	24.6885	23.9843	2.2325	2.6693	3.0532	0.0984	0.1547	0.2098
0.004	25.8315	24.7264	24.0343	2.2240	2.6592	3.0388	0.1340	0.1927	0.2598
0.005	25.8684	24.7317	24.0594	2.2161	2.6593	3.0311	0.1709	0.1979	0.2850
<b>Water + ALS 7mM + sodium silicate</b>									
0	25.7186	24.5706	23.6932	2.2157	2.6631	3.1080	-	-	-
0.001	25.8019	24.2575	23.7869	2.1998	2.6400	3.0850	0.0833	0.0858	0.0937
0.002	25.8110	24.2857	23.8423	2.2018	2.6369	3.0687	0.0924	0.1139	0.1491
0.003	25.8325	24.3320	23.8721	2.1979	2.6228	3.0588	0.1139	0.1603	0.1789
0.004	25.8704	24.3637	23.9048	2.1905	2.6131	3.0483	0.1518	0.1920	0.2116
0.005	25.9039	24.3749	23.9443	2.1832	2.6123	3.0365	0.1853	0.2031	0.2511

### Internal pressure ( $\pi_i$ ):

In the study of thermodynamic properties, the measurement of internal pressure is an important parameter.  $\pi_i$  are the resultant force of attraction and the force of repulsion between the molecules in a solution. The internal pressure of aqueous ALS (table 3) is found to be increase with increase in molarity of sodium silicate. This is because of the internal molecular association of ALS with sodium silicate ions. Aqueous ALS solution creates, a stronger cohesive force in it, which increase the internal pressure. At a particular concentration,  $\pi_i$  decrease with temperature is found for all the systems. It is noted that  $\pi_i$  decrease at 313K. This may be due to volume expansion and the molecules move away from each other causes to reduce ion pairing, so that the repulsive force become predominant and ultimately leads to decrease in internal pressure (Suryanarayana C.V., 1992) [23].

### Free volume ( $V_f$ ):

Eying and Kincaid defined the free volume as an effective volume in which particular molecules of the liquid can move and obey perfect gas laws. The molecular interactions between like and unlike molecules are influenced by structural arrangements along with shape and size of the molecules. The molecules of a liquid are not quite closely packed as there are some free spaces between the molecules for movement and at volume are called free volume  $V_f$  (Eying .H., 1983) [24].

The values of free volume of silicate solutions are given in table 3.  $V_f$  of ALS solution shows an increase in  $V_f$  with increase in temperature and decreases with rise in molarity of sodium silicate and ALS. As the concentration of sodium silicate increases the molecules of ALS are closely packed and there is no free space between them thus  $V_f$  decreases. When the temperature rises, there is a drift for ions to move away from each other which reduce the probability for interactions which may reduce the cohesive forces and adhesive forces which leads to increase in free volume.

### Change in internal pressure ( $\Delta\pi_i$ ):

The change in internal pressure ( $\Delta\pi_i$ ) predicts that the value can be positive or negative depends on the nature of the solute. It is observed from table 3 that  $\Delta\pi_i$  increases with increase in sodium silicate and ALS molarities with temperatures. This may be due to the hydrophobic group composed by a concentric shell of hydrophilic head group with counter ion. The ammonium counter ions neutralized the charge of micelles and bound with them which enhance the internal pressure of the ALS solution. On the other hand,  $\Delta\pi_i$  decreases this may due to volume expansion. The impacts of

thermal energy in the aqueous ALS and sodium silicate solution, which cause more frequently and exerting an internal energy to reduce the internal pressure. The positive values of  $\Delta\pi_i$  indicate that sodium silicate act as a structure maker.

### Relation between internal pressure and free volume with temperature:

C.V. Suryanarayana and Kuppaswamy (1981) [25] established the quantitative relations between variations of internal pressure and free volume.

$$\pi_i = \pi_0 + Am^2 + Bm \quad (6)$$

where  $\pi_0$ , is the internal pressure of the aqueous ALS,  $m$  is the molarity of sodium silicate,  $A$  and  $B$  are arbitrary constants dependent on temperature.

A similar relation retain for the free volume,

$$V_f = V_{f(0)} + Cm^2 + Dm \quad (7)$$

The free volume constants  $C$  and  $D$  are dependent on temperatures.

$\Delta\pi_i = \pi_i - \pi_0$ , is the difference in the internal pressure of the solution, and the solvent can be positive or negative depends on the electrolyte. In all the systems,  $\Delta\pi_i$  is positive. Coefficient  $A$  refers to the attractive component and  $B$  refers to the repulsive component and determines the sign of  $\Delta\pi_i$  (Ramaprabha S, 2017) [26]. Internal pressure of the solution increases progressively according to the relation (6).

The values of constants  $A$  and  $B$  are computed and are given in table 4. The values of  $A$  are negative. Since the magnitude of  $A$  is very small and does not affect the progressive variation of internal pressure with concentration. The addition of solute creates cohesive force and thus the ions of sodium silicate are easily bonded with hydrogen and interacted with hydrophilic part of ALS molecules.  $B$  values are found to be positive and hence  $\Delta\pi_i$  positive indicating the internal pressure of the solvent increases due to the addition of sodium silicate.

The free volume of the solutions decreases with increase in concentration of sodium silicate and ALS according to the relation (7). The values of constants  $C$  and  $D$  are computed for different temperature and are given in table-4 and represented graphically (fig 4 and 5). In all the ALS solutions it is found that  $C$  is positive and  $D$  is negative at all temperatures. In 4mM and 5mM ALS solutions  $C$  increases with temperature and is minimum at 313K in the case of 7mM ALS.  $D$  is found to decrease with temperature in all the solutions.

**Table 4: A, B, C, D values of sodium silicate in three different concentrations of ALS**

Temp K	Internal Pressure Constants		Free Volume Constants	
	A*10 <sup>-10</sup>	B*10 <sup>-10</sup>	C*10 <sup>-8</sup>	D*10 <sup>-8</sup>
<b>4mM ALS + Sodium silicate</b>				
303	-52.4873	0.5434	0.0015	-5.9574
308	-86.4927	0.7889	0.0025	-9.2193
313	-127.748	1.1751	0.0294	-20.785
<b>5mM ALS + Sodium silicate</b>				
303	-55.6067	0.5680	0.0078	-8.0442
308	-89.3602	0.8103	0.0146	-10.535
313	-121.427	1.1015	0.0259	-19.360
<b>7mM ALS + Sodium silicate</b>				
303	-100.725	0.7871	0.0195	-8.3862
308	-99.3549	0.8678	0.0266	-14.545
313	-91.8155	0.9201	0.0078	-16.969

Figure 2 and figure3 shows the temperature dependence of A and B. A is found to decrease linearly with temperature in the case of 4mM and 5mM ALS solutions. In 7mM ALS solution, A is found to increase with temperature and is reflected in the value of internal pressure. B shows positive values and increases with temperature in all the solutions. The variation of B with temperature is opposite to that of A.

From this investigation it is clearly found that attractive component A is reverse to that of free volume constant C, repulsive component B is reverse to that of D. This observation forties that free volume is reverse to that of internal pressure in sign and magnitude.

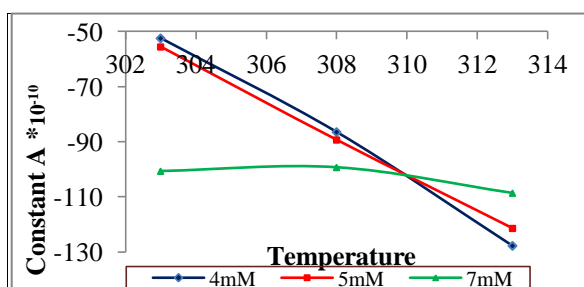


Fig 2 Variation of constant A with temperature

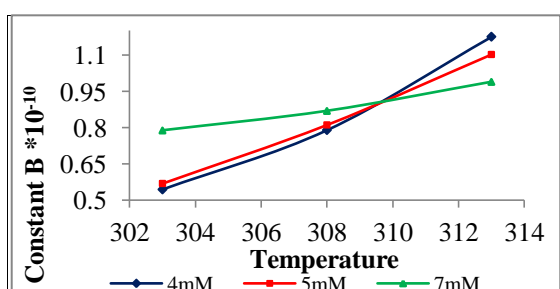


Fig 3 Variation of constant B with temperature

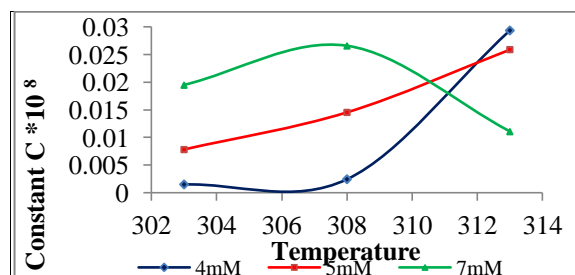


Fig 4 Variation of constant C with temperature

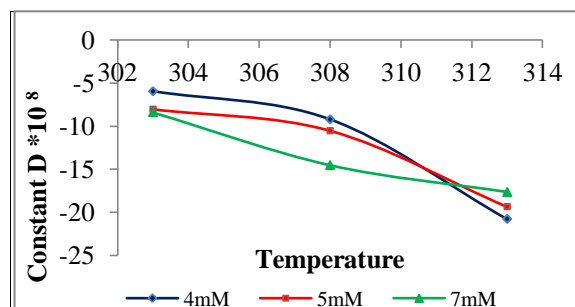


Fig 5 Variation of constant D with temperature

## 5. Conclusion

The experimental data of density, viscosity and ultrasonic velocity at three different temperatures for sodium silicate in three different concentration of ALS are reported. From this observation the acoustic and thermodynamic parameters are calculated and inter molecular interaction between water (H<sup>+</sup> and OH<sup>-</sup>), sodium silicate (Na<sub>2</sub><sup>+</sup> and SiO<sub>3</sub><sup>-</sup>) and ALS (hydrophilic and hydrophobic) have been studied. The qualitative relations of π<sub>i</sub> and V<sub>f</sub> with temperature predicts the nature of sodium silicate in ALS. The results suggested that builder sodium silicate promotes structure making capacity which enhances the detergent efficiency of anionic surfactant ALS. The results from the ultrasonic study which shows the efficiency of sodium silicate in ALS is in the order 7mM > 5mM > 4mM. Thus, 7mM of ALS has distended hydrophobic interaction and micelles formation and the other two concentrations were minimal. The above finding clearly shows that the detergent action of anionic surfactant ALS can be enhanced considerably by the addition of sodium silicate. The efficiency is greater in 7mM ALS.

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