# INTERNAL PRESSURE AND FREE VOLUME OF SODIUM HYPOCHLORITE IN AQUEOUS ANIONIC SURFACTANT

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***Abstract:***

The thermodynamic behaviour of sodium hypochlorite (Bleach) in anionic surfactant ammonium lauryl sulphate (4mM, 5mM, & 7mM) with different concentrations and temperatures are studied. Anionic surfactant (ALS) is wetting the fabric easily by spreading and lowering the interfacial tension between the liquid mixtures. Sodium hypochlorite acts as a bleaching agent in detergents and textile industries. The internal pressure, free volume and change in internal pressure were calculated by using the experimental values of ultrasonic velocity ($U$), density ($\rho$) and viscosity ($\eta$) of the solutions**.** The variation between internal pressure and free volume with concentration and temperatures are evaluated to support this study. The impacts of surfactant solution added soil were analyzed by the measured values of physical properties like soil color, soil texture and chemical properties such as pH, EC, macro and micro nutrients of the soil. The results observed from ultrasonic studies and soil analyses are agreed well with each other.

***Keywords:***

Internal pressure, free volume, soil texture, pH, macro and micro nutrients

## I. INTRODUCTION:

Ultrasonic technique is a great tool to study the properties of liquid and mixed solution. This technique is used to determine the nature and strength of interaction between molecules in solutions. It provides valuable information about solute-solvent, solvent-solvent, solute-solute interactions in the liquid mixtures [1-5]. The study of thermodynamic properties predicts the behavior of molecular association and understands the interior composition of solute and solvents molecules.

Laundry detergents contain surfactant with other formulated components to enhance the behavior of detergent to remove the stains from the fabric interface [6]. Surfactants have two different regions according to their chemical structure; one is water liking or hydrophilic (polar head) and other of which is water fearing or hydrophobic (non-polar tail end). These are referred as amphiphilic molecules. Surfactant solution may contain an ordered micelle phase, a disorder phase of free surfactant molecules and ions in the solution.

Ammonium lauryl sulphate (ALS) is an anionic surfactant depends on their negative charge of the surface active hydrophilic head group molecule. Ammonium lauryl surfactant is a liquid detergent which is easily soluble in water, dissociated into $CH_3(CH_2)_{11}OSO_3^-$ lauryl sulphate anion and ammonium cation $NH_4^+$ (counter ion) and act as an effective and efficient cleaning by removing tough stains. It is also used as skin cleansers, cosmetics and an excellent foaming agent [7]. Sodium hypochlorite is the most important ingredient in laundry detergent. It is particularly more effective to remove stains easily in cotton fibers, brighten the clothes and performs as disinfectant on fabric. The main purposes of bleaches are act as an oxidizer in laundry detergents [8].

Soil is an important part of the natural ecosystem. It is made of minerals, nutrients, water, air, organic matter and micro organism [9]. These components are important factors for nutrient management. Soil has vital role in agriculture to nourish nutrients for plants. The roots of plant receive water and nutrients from soil to help the plants growth.

Soil analysis is the processes to determine the physical and chemical properties of soil health. The properties of soil are used to evaluate the status of nutrients present in soil and predict the required amount of fertilizer for the crop production. The physical properties of the soil viz., colour, texture and chemical properties viz., pH, EC, macro and micro nutrients available in soil are crucial for crop cultivation. The variation of internal pressure and free volume of sodium hypochlorite with respect to concentration and temperature were analyzed. Sandy clay loam soil taken from Kulavaipatti village, Pudukkottai district was used for this investigation.

## II. EXPERIMENTAL TECHNIQUES:

Ammonium lauryl sulphate (Sigma Aldrich Chemicals) from USA and liquid sodium hypochlorite (Chlorine bleach) from Merck, Mumbai were taken. Deionized water was used for solution preparation. 10ml specific gravity bottles (with accuracy of $\pm 0.1 Kg.m^{-3}$) were used to measure the density of solution. Viscosities of the solutions are measured using an Ostwald′s viscometer (10ml capacity). The time flow is measured by Racer stop watch with an accuracy of ± 0.01s. Ultrasonic velocity of solutions was measured by a single crystal (Mittal F−81) ultrasonic interferometer of fixed frequency of 2 MHz. Electronic constant temperature bath is used to maintain the desired temperature with ±0.1°C precision. 300gm of soil was taken and was kept in a container for 10 days. When the soil was completely dried then the soil samples were taken for soil analysis.

## III. FORMULATION:

The internal pressure ($\pi_i$) and free volume ($V_f$) of the solutions have been evaluated by the following relations,

$$\text{Internal pressure} \qquad \pi_i = bRT\left[\frac{k.\eta}{U}\right]^{\frac{1}{2}}.\frac{\rho^{2/3}}{M^{7/6}} \qquad \text{-------- (1)}$$

Free volume $V_f = [\frac{U.M_{eff}}{\eta.k}]^{3/2}$ -------- (2)

where, b stands for cubic packing factor, R is a gas constant (8.314 K.J $mol^{-1}$); T is absolute temperature; k is temperature dependent constant (4.28 x $10^9$); $M_{eff}$ is effective molecular weight of the surfactant solution.

## IV. RESULT AND DISCUSSION:

The estimated values of internal pressure and free volume are noteworthy to explain the variation of interactions in solution. Internal pressure is the measurement of attractive force of molecules which creates cohesion in solution. Free volume is an effective volume in which a particular molecule can move in an average potential due to the repulsion of its neighboring molecules [10]. The study of density, viscosity and ultrasonic velocity parameters are required to understand the interesting features about solute-solvent, solute-co-solute, solvent-co-solute and the intermolecular interactions in the solution.

From table (1), the internal pressure of sodium hypochlorite increases with increase in the concentration of aqueous ALS (4mM, 5mM & 7mM). This indicates the structure making capacity of solute molecules**.** When sodium hypochlorite is dissolved in aqueous ALS solution, it splits up into sodium ($Na^+$) ions and hypochlorite ($ClO^-$) ions. These ions are interacted with lauryl sulphate anion and ammonium cation which creates a greater cohesion due to electrostrictive force. This electrostrictive effect brought shrinkage in volume of solvent molecules caused by solute ions and due to increase in density.

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

Internal pressure ($\pi_i$) of sodium hypochlorite is minimum for 7mM ALS at all temperatures [11]. This minimum value denotes that, when the temperature is increased the mobility of solute ions and solvent molecules move away from each other due to increase of velocity and energy, which reduce the possibility of interaction. Thus velocity increases accordingly the pressure decreases [12]. $\pi_i$ of ALS decreases this may be due to the increase in more number of micelle formations.

### 4.2 Free volume ($V_f$):

Free volume of sodium hypochlorite in aqueous ALS decreases with increase of concentration at all temperatures. This is due to the increase in viscosity that shows the closer packing of solvent molecules with the addition of solute at these temperatures [13-14]. Thus $V_f$ shows an increasing trend with increases in temperature at all ALS concentrations. This decreasing and increasing variation of $V_f$ confirms the structure making and breaking properties of solute. From these result it is noted that the variation of $\pi_i$ and $V_f$ are inversely related [15].

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

| Molarity M | Internal Pressure($\pi_i$) $10^8$ $Nm^{-2}$ | | | Free Volume ($V_f$) $10^{-8}$ $m^3mol^{-1}$ | | | Change in Internal Pressure $\Delta\pi_i$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | 303K | 308K | 313K | 303K | 308K | 313K | 303K | 308K | 313K |
| **4mM ALS + Sodium hypochlorite** | | | | | | | | | |
| 0 | 25.6241 | 24.3271 | 23.8314 | 2.2863 | 2.7874 | 3.1049 | -0.1840 | -0.5297 | -0.1723 |
| 0.001 | 25.5131 | 24.2940 | 23.8269 | 2.3242 | 2.8120 | 3.1223 | -0.1111 | -0.0330 | -0.0045 |
| 0.002 | 25.5644 | 24.3538 | 23.8771 | 2.3171 | 2.7967 | 3.1087 | -0.0597 | 0.0268 | 0.0457 |
| 0.003 | 25.5962 | 24.3768 | 23.9029 | 2.3126 | 2.7954 | 3.1051 | -0.0279 | 0.0498 | 0.0715 |
| 0.004 | 25.6314 | 24.4499 | 23.9633 | 2.3085 | 2.7786 | 3.0914 | 0.0073 | 0.1228 | 0.1319 |
| 0.005 | 25.6765 | 24.4712 | 24.0244 | 2.3003 | 2.7772 | 3.0759 | 0.0524 | 0.1441 | 0.1930 |
| **5mM ALS + Sodium hypochlorite** | | | | | | | | | |
| 0 | 25.6975 | 24.5338 | 23.7745 | 2.2525 | 2.7002 | 3.1070 | -0.1106 | -0.3230 | -0.2292 |
| 0.001 | 25.5179 | 24.4338 | 23.7311 | 2.3071 | 2.7437 | 3.1371 | -0.1797 | -0.1000 | -0.0433 |
| 0.002 | 25.6006 | 24.5121 | 23.7718 | 2.2891 | 2.7228 | 3.1283 | -0.0969 | -0.0217 | -0.0026 |
| 0.003 | 25.6520 | 24.5407 | 23.7943 | 2.2820 | 2.7206 | 3.1257 | -0.0455 | 0.0069 | 0.0199 |
| 0.004 | 25.6736 | 24.5767 | 23.8583 | 2.2803 | 2.7169 | 3.1099 | -0.0240 | 0.0429 | 0.0839 |
| 0.005 | 25.7190 | 24.6388 | 23.8991 | 2.2725 | 2.7033 | 3.1022 | 0.0215 | 0.1050 | 0.1246 |
| **7mM ALS + Sodium hypochlorite** | | | | | | | | | |
| 0 | 25.7186 | 24.5706 | 23.6932 | 2.2157 | 2.6631 | 3.1080 | -0.0896 | -0.2862 | -0.3105 |
| 0.001 | 25.3888 | 24.3396 | 23.5886 | 2.3108 | 2.7495 | 3.1636 | -0.3298 | -0.2310 | -0.0467 |
| 0.002 | 25.4662 | 24.3941 | 23.6172 | 2.2944 | 2.7363 | 3.1569 | -0.2524 | -0.1765 | -0.0155 |
| 0.003 | 25.4914 | 24.4531 | 23.6483 | 2.2924 | 2.7233 | 3.1525 | -0.2272 | -0.1175 | 0.0156 |
| 0.004 | 25.5176 | 24.4698 | 23.6784 | 2.2891 | 2.7224 | 3.1456 | -0.2011 | -0.1008 | 0.0458 |
| 0.005 | 25.5373 | 24.4866 | 23.7204 | 2.2855 | 2.7207 | 3.1344 | -0.1813 | -0.0840 | 0.0877 |

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

$\Delta\pi_i = \pi_i - \pi_0$ is the change in internal pressure of solution may be positive or negative depends upon the strength and nature of the solute. $\Delta\pi_i$ increases with increase in the solute concentration and temperatures is given in table1. This may be due to weakening of cohesive force by breaking solute–solvent molecules. $\Delta\pi_i$ decreases with increase in ALS concentration which indicates repulsive force of ALS which predominant the solute ions. The positive $\Delta\pi_i$ predicts the structure making tendency of sodium hypochlorite. Negative $\Delta\pi_i$ denotes the structure breaking capacity of ALS and it is more in 7mM ALS solution.

### 4.4 Quantitative relation of internal pressure and free volume with temperature:

Suryanarayana C.V and Kuppuswamy (1981) [16] found the relation for internal pressure with concentration is given by,

$$\pi_i = \pi_0 + Am^2 + Bm$$

where, $\pi_0$ in the internal pressure of aqueous ALS, m is molarity of sodium hypochlorite. A and B are the temperature depended constants. The coefficients A and B are the attractive and repulsive components.

A coefficient is found to be positive for all three ALS concentrations. The addition of sodium hypochlorite may be easily bonded with water and ALS molecules. This interaction causes a strong attractive force and hence the magnitude of A is higher in the order of 7mM>5mM>4mM. The coefficient of B determines the sign of $\Delta\pi_i$ and it is found to be negative for all the systems**.** It is observed from table (3) that B value is dominant in 7mM ALS solution.

**Table 2: A, B, C, D values of sodium hypochlorite in three different concentrations of ALS**

| Temperature K | Internal Pressure Constants | | Free Volume Constants | |
|---|---|---|---|---|
| | Constant A $10^{10}$ | Constant B $10^{10}$ | Constant C $10^{8}$ | Constant D $10^{8}$ |
| **Water+ ALS 4mM+ Sodium Hypochlorite** | | | | |
| 303 | 274.76 | -1.10 | -7.999 | 38.08 |
| 308 | 141.04 | -0.31 | -6.02 | 23.61 |
| 313 | 95.06 | -0.06 | -5.16 | 17.51 |
| **Water+ ALS 5mM+ Sodium Hypochlorite** | | | | |
| 303 | 410.35 | -1.72 | -11.25 | 52.47 |
| 308 | 263.62 | -0.94 | -9.29 | 41.14 |
| 313 | 185.00 | -0.56 | -7.21 | 30.98 |
| **Water+ ALS 7mM+ Sodium Hypochlorite** | | | | |
| 303 | 663.04 | -3.23 | -18.32 | 93.42 |
| 308 | 491.20 | -2.27 | -17.15 | 85.33 |
| 313 | 259.58 | -1.10 | -15.36 | 37.26 |

A similar relation available for free volume is

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

where, $V_{f(0)}$ is the free volume of solvent, C and D constants are dependent on temperature. The values of C coefficient are found to be negative for all ALS solutions and D is positive at all temperatures are listed in table (3). The C value increases with temperature and decreases with ALS concentration and it is in the order of 4mM>5mM>7mM. The D coefficients are reverse to C.

The quantitative relation of $\pi_i$ and $V_f$ with concentration predicts that the fetching component of internal pressure A is reverse to that of free volume coefficient C, the repellent component B is reverse to that of D coefficient which are show in figures 1-4. From this result, it was confirmed that internal pressure is reverse to that of free volume in magnitude and sign [17].

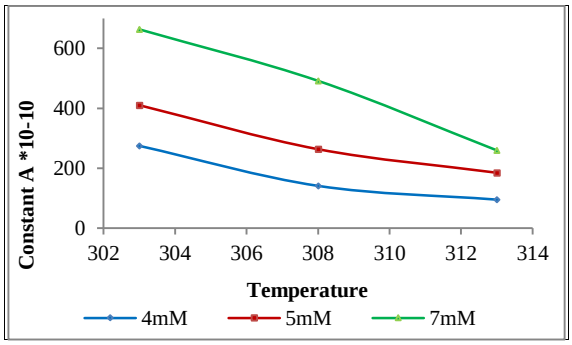


**Fig 1 Variation of constant A with temperature**

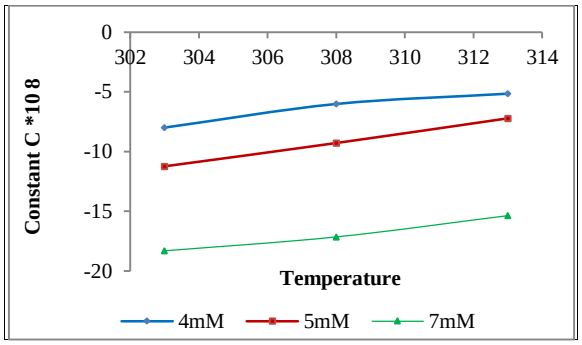


**Fig 3 Variation of constant C with temperature**

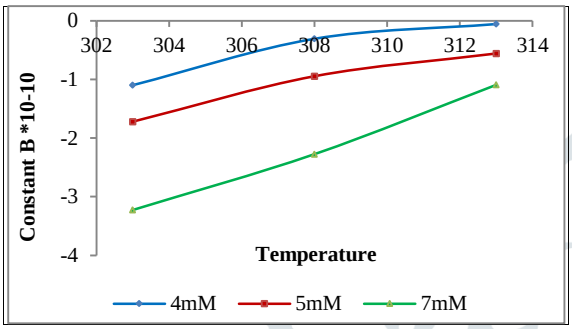


**Fig 2 Variation of constant B with temperature**

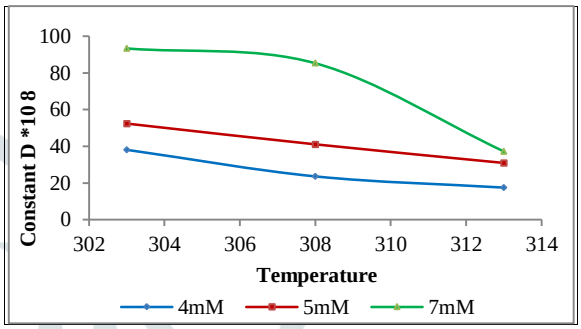


**Fig 4 Variation of constant D with temperature**

## V. SOIL ANALYSIS:

Soil is the thin layer found on the surface of earth. It is composed of organic matter that provides the medium for the growth of plants. Soil properties may affect plant growth and nutrition management.

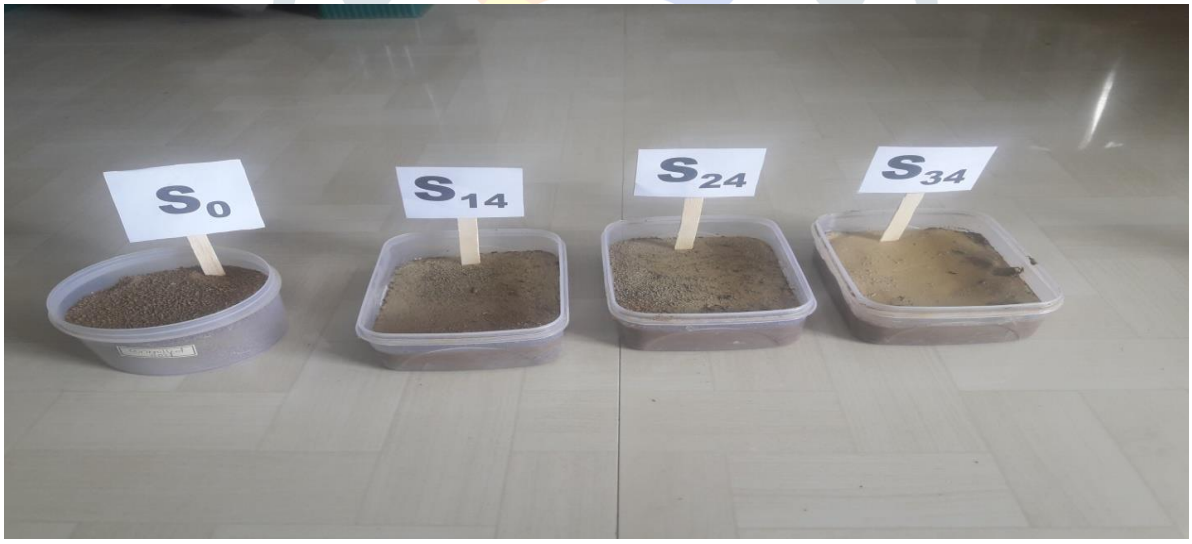


**Fig 5 Photography of controlled soil, 4mM, 5mM and 7mM aqueous ALS with 0.03mM sodium hypochlorite**

### 5.1 Soil colour:

Soil colour is an indirect measurement of various properties of soil**.** Sandy clay loam soil is taken for this study, which is yellowish brown colour**.** This type of soil has good air-water relation and rich in iron–oxide [18].

### 5.2 Soil texture:

Soil texture is described by the size of the individual particles of the soil. The proposition of soil is sand, silt and clay**.** The texture of sandy clay loam (SCL) soil is composed of 50% of sand, 30% of clay and 20% of silt [19].

**Table 3: Physical and chemical properties of the soil for sodium hypochlorite in ALS solutions**

| **Physical Properties** | **Soil color** | | Yellowish Brown | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **Soil texture** | | **Sandy clay loam** (Sand - 50-80%; Silt - 0-30%; Clay - 20-30%) | | | | | | |
| **Chemical Properties** | | | **Macro nutrients** | | | **Micro nutrients** | | | |
| **Sample** | **pH** | **EC** $dsm^{-1}$ | **N** Kg/acre | **P** Kg/acre | **K** Kg/acre | **Fe** | **Mn** | **Zn** | **Cu** |
| **$S_0$** | 7.5 | 0.13 | 58.8 | 6.0 | 47.0 | 4.491 | 3.968 | 0.608 | 0.564 |
| **$S_{14}$** | 6.52 | 0.22 | 116.2 | 4.5 | 47.0 | 4.569 | 3.396 | 0.741 | 0.746 |
| **$S_{24}$** | 6.67 | 0.30 | 91.0 | 4.5 | 67.0 | 4.696 | 3.460 | 0.686 | 0.568 |
| **$S_{34}$** | 6.6 | 0.27 | 88.2 | 6 | 70.0 | 4.8 | 3.498 | 0.687 | 0.858 |

**$S_0$** - Controlled Soil; S14 - 4mM ALS + 0.03mM sodium hypochlorite; **$S_{24}$** - 5mM ALS + 0.03mM sodium hypochlorite; **$S_{34}$** - 7mM ALS + 0.03mM sodium hypochlorite

### 5.3 Soil pH:

The pH of soil determines the value of acid or alkali present in the soil, which influences the availability and maintains the nutrients for plant and root growth. The pH value around 5.0–8.5 is feasible for plant growth production [20]. The variation of pH values with controlled soil and surfactant solution added soil are shown in table 3. It is important to note that the pH of controlled soil is 7.5 and the surfactant added soils decreases up to 6.5. This indicates the pH value is slightly neutral and feasible for plant growth.

### 5.4 Electrical conductivity (EC):

EC is a measure of salinity present in the soil and indicates the soil′s health. EC value is less than one $dsm^{-1}$, this type of soil is non–saline which increase the plant growth and do not affect the microbial activity [21]. For all samples EC values are less then $1dsm^{-1}$, which reduces the nitrogen loses and increase the population of micro organism.

### 5.5 Macronutrients:

The macro nutrients N, P, K are required in large amounts for the plants to grow, survive and production. The three big major nutrients NPK are also called “fertilizer elements”. Nitrogen is one of the important nutrients which promotes plant growth and increase the chlorophyll molecules for the growth of leaf quality.

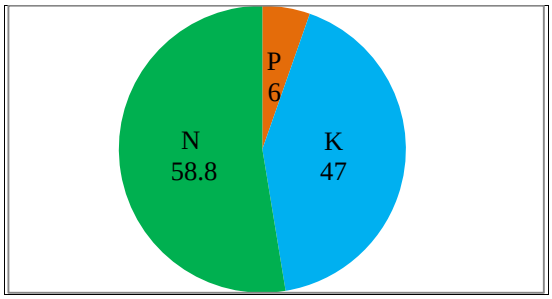


**Fig 6 Macro Nutrients of controlled soil**

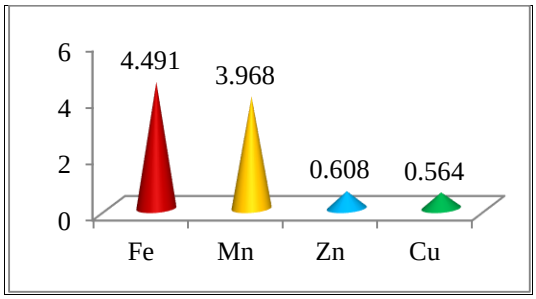


**Fig 10 Micro Nutrients of controlled soil**

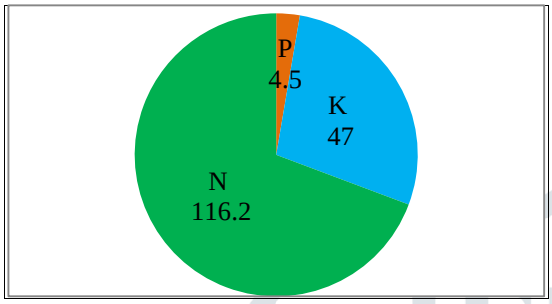


**Fig 7 Macro Nutrients of 4mM aqueous ALS with 0.03mM sodium hypochlorite**

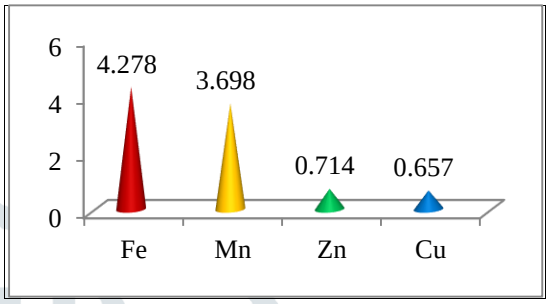


**Fig 11 Micro Nutrients of 4mM aqueous ALS with 0.03mM sodium hypochlorite**

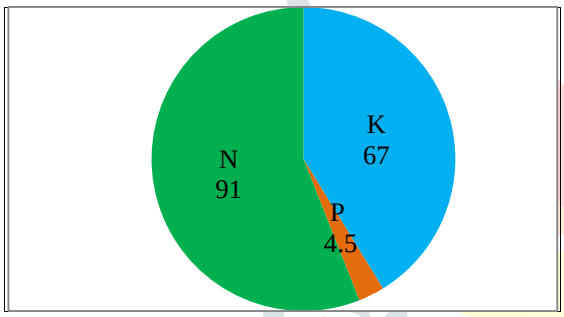


**Fig 8 Macro Nutrients of 5mM aqueous ALS with 0.03mM sodium hypochlorite**

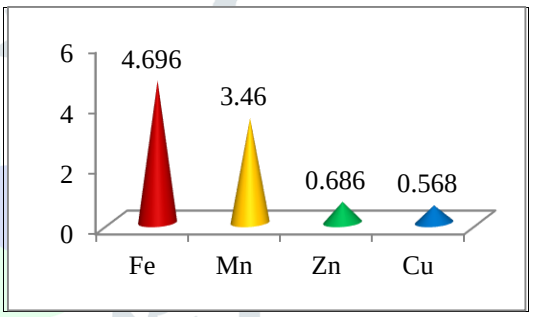


**Fig 12 Micro Nutrients of 5mM aqueous ALS with 0.03mM sodium hypochlorite**

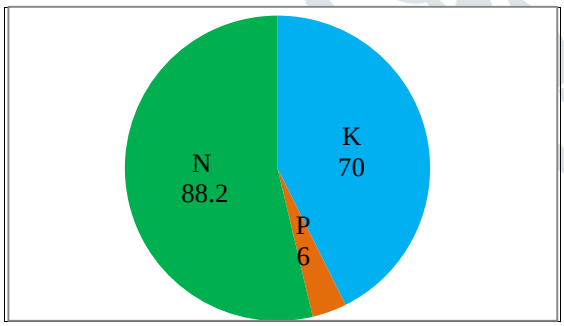


**Fig 9 Macro Nutrients of 7mM aqueous ALS with 0.03mM sodium hypochlorite**

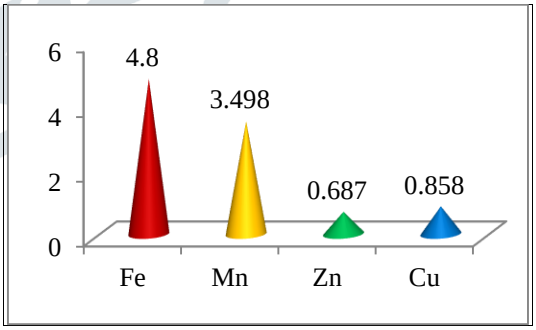


**Fig 13 Micro Nutrients of 7mM aqueous ALS with 0.03mM sodium hypochlorite**

Phosphorous promotes the development of seed, root and vigorous growth where as potassium reduces diseases, improve seed quality. The result observed from the table 3 fortifies that nitrogen value is higher in surfactant added soil than controlled soil.

The increases in surfactant concentration decrease the nitrogen value these affects the quality of leaf whereas potassium value increases. These indicate that potassium improves the seed quality and reduces the

plant diseases. The value of nitrogen is higher in 4mM ALS whereas potassium is higher in 7mM ALS. Phosphorous take part in low level which is due to the deficiency of manganese (Mn). There is a strong relationship between phosphorus and zinc. The high values of phosphorus will consistently reduce Zn uptake and excess value of Zn will have same effect on phosphorus. The standard ratio of P/Zn is 10:1 in sustain of phosphorus [22]. This ratio is achieved in controlled and 7mM ALS added soil which indicates maximum performance of both P and Zn minerals.

**5.6 Micronutrients:**

Micronutrients copper (Cu), manganese (Mn), iron (Fe) and zinc (Zn) are cations which may associate with organic matter and required for plant growth in trace amount. Copper and Manganese is necessary in photosynthesis, nitrogen metabolism and plant metabolism. Zinc is one of the essential nutrients for enzyme systems, protein synthesis and also for plant growth regulation. Iron is involved in the production of chlorophyll and leaf chlorosis. In soil analysis Fe should always be higher than Mn to avoid iron lockups. Excess Fe may limit Mn uptake and vice versa. Zn is high in 4mM ALS solution and Mn is more in controlled soil. 7mM ALS surfactant solutions have high Fe and Cu than controlled and other surfactant added soil.

From this analysis the surfactant added soil has sufficient nutrients content than controlled soil and it is appeared clearly in figures (6-13). This treatment soil samples are feasible for plant growth.

**Conclusion:**

The molecular interactions of sodium hypochlorite (chlorine bleach) with ammonium lauryl sulphate (ALS) anionic surfactant solution have been studied. The variation of internal pressure and free volume with concentration and temperature are evaluated. The results of quantitative relation between $\pi_i$ and $V_f$ shows the structure breaking and making tendency of sodium hypochlorite ions in aqueous ALS solutions. pH, EC, macro and micronutrients of surfactant added soil have a good balance of nutrients for the growth of plants. The ultrasonic studies emphasizes the interactions in the order 7mM>5mM>4mM. This result is confirmed by soil analysis.

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