RESEARCH ARTICLE

THERMODYNAMICAL PROPERTIES OF SODIUM CHLORIDE IN AQUEOUS CETYL TRIMETHYL AMMONIUM BROMIDE SOLUTION USING ULTRASONIC STUDY.

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Abstract

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The thermodynamical behaviour of sodium chloride in aqueous cetyltrimethyl ammonium bromide (CTAB) solution at 303K, 308K and 313K is studied. Density (ρ), viscosity (η) and ultrasonic velocities (U) of the solutions are measured experimentally at different concentrations of sodium chloride. For this, aqueous solutions of CTAB are prepared at three molarities (0.2mM, 0.3mM and 0.4mM). By knowing the experimental values, the internal pressure (π_i) and free volume (V_f) of the solutions are determined. From these values quantitative relations between internal pressure, free volume with concentration of these solutions are verified. The results show that sodium chloride existing in aqueous cetyltrimethyl ammonium bromide act as structure-breaker. $\Delta\pi_i$, A, B values of internal pressure, C, D values of free volume and viscosity B-coefficient of Jones-Dole equation are also evaluated to support the present study.

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Introduction:-

Surfactants play an important role as cleaning, wetting, dispersing and emulsifying, foaming and anti-foaming agents in many practical applications. Surfactants are usually organic compounds that are amphiphilic, i.e., they contain both hydrophobic groups (their tails) and hydrophilic groups (their heads). Therefore, a surfactant contains both a water-insoluble component and a water soluble component. Surfactant is a compound that lower the surface tension of a liquid, the interfacial tension between two liquids that between a liquid and soap. Surfactant molecules will migrate to the water surface, where the insoluble hydrophobic group may extend out of the bulk water phase, either in to the air or, in to the oil phase, while the water soluble head group remains in the water phase. This alignment and aggregation of surfactant molecules are at the water/air or water/oil interface. Surfactants are generally classified on the basis of their ionic properties such as anionic, cationic, non-ionic and Zwitterionic surfactants.

Among them, the surfactant chosen for present study is cationic surfactant (CTAB). Cations are formed in reactions where alkyl halides react with primary, secondary, or ternary amines. In this type of surfactant, the water-soluble part of the molecule has a positive charge and the water-insoluble part of the molecule is hydrocarbon, thus giving in the name of a cationic surface active agents. Cetrimonium ($C_{19}H_{42}BrN$) or (cetyltrimethyl ammonium bromide) cation is an effective antiseptic agent against bacteria and fungi. It is also one of the main components of the buffer for the extraction of DNA [1]. Detergent fillers are the materials, which are added in detergents to alter their physical

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characteristics and properties. Sodium chloride is one of the important filler used in detergents. It is used as water softening agent, and to standardize their level in the detergent.

Ultrasonic has become the most inspiring and delighting field of scientific research among the researchers. The ultrasonic parameters provide useful information regarding the molecular packing. The observed and calculated thermodynamical parameters are used to explain molecular association, complex formation and solute-solvent interactions. Literature survey shows that ultrasonic velocity, density, viscosity and allied thermodynamic parameters play a key role to study the nature of intermolecular forces in liquid solutions and the physico-chemical behaviour of liquid mixture [2].

In the present work, thermodynamic properties of CTAB (0.2mM, 0.3mM and 0.4mM) with NaCl at different concentrations (0.1M to 0.5 M) and different temperatures are studied.

Experimental method:-
Aqueous solutions of CTAB (0.2mM, 0.3mM and 0.4mM) were prepared and used on the day they were prepared. Solutions of sodium chloride of various concentrations from 0.1M to 0.5M are prepared on the molarity concentrations scale using Denver electric digital balance with a precision of $\pm 1 \times 10^{-4}$ g.

The ultrasonic velocities of the solutions were measured with an accuracy of $\pm$ 0.5% using an ultrasonic interferometer (Mittal Enterprises, New Delhi, Model: F-81) with a single crystal operating at a frequency of 2MHz. The density of solutions was measured using a 10 ml specific gravity bottle with an accuracy of $\pm$ 0.1 Kg m^{-3}. Ostwald's viscometer of 10 ml capacity was used for viscometric studies. The time flow was measured using a racer stop watch with an accuracy of $\pm$ 0.1sec. A constant temperature bath (RAAGA Industries, Chennai) which could maintain temperature within $\pm$ 0.1°C is used throughout the experiment.

Theory and calculation:-
Using the measured values of density, viscosity and velocity, the internal pressure and free volume are evaluated using standard formulae.

Internal Pressure (π_i):-
The internal pressure is the cohesive forces, which is the resultant forces of attraction and forces of repulsion between the molecules.

$$\pi_i = bRT \left(\frac{K\eta}{U}\right)^{1/2} \left(\frac{\rho^{2/3}}{M^{7/6}}\right) \qquad \text{Nm}^{-2} \quad (1)$$

b stands for cubic packing, which is assumed to be 2 for all liquids. K is a dimensional constant independent of temperature and nature of liquids. Its value is 4.281×10^9, T-absolute temperature in Kelvin, M-effective molecular weight, R-universal gas constant, η-viscosity of solution in Nsm^{-2}, U-ultrasonic velocity in ms^{-1} and ρ-density of solution in Kgm^{-3}.

Free volume (V_f):-
Free volume is defined as the average volume in which the centre of the molecules can move inside the hypothetical cell due to the repulsion of surrounding molecules. The dimensional relation given by C.V. Suryanarayana and Kuppusamy[3] which is based on the viscosity and ultrasonic velocity data as,

$$V_f = \left(\frac{M_{eff}U}{K\eta}\right)^{3/2} \qquad \text{m}^3 \qquad (2)$$

Change in the internal pressure:-
Change in internal pressure $(\Delta\pi_i)$ is defined as difference between the internal pressure of solvent and solution. Change in internal pressure may be used to interpret the structural behaviour of the solute towards the solvent. Depending upon its sign and nature, the ions can be classified as structure maker and structure breaker.

$$\Delta\pi_i = \pi_i - \pi_0 \qquad (3)$$

Quantitative relationship between internal pressure and free volume dependent on concentration:-
Suryanarayana C.V and Kuppusami found a relation between internal pressure and free volume at a given temperature of the form

$$\pi_i = \pi_0 + Am^2 + Bm \qquad (4)$$

where, π_0 is the internal pressure of the solvent, m is the molarity, holds good not only for all electrolytes but also with glucose[4]. The constants A and B are dependent on temperature.

A similar relation holds for the free volume

$$V_f = V_{f(0)} + Cm^2 + Dm \qquad (5)$$

Here, $V_{f(0)}$ is the free volume of the solvent. The arbitrary coefficients C and D are dependent on temperature.

Relation between viscosity and concentration:-
A and B coefficients of viscosity for the surfactant solutions were calculated from the Jones-Dole equation [5]

$$\frac{\eta}{\eta_0} = 1 + Am^2 + Bm \qquad (6)$$

where η is the viscosity of the solution, η_0 is the viscosity of the solvent and m is the molar concentration of the solute. A is determined by ionic attraction theory of Falkenhagen-Vernon and therefore called as Falkenhagen co-efficient [6], B is Jones-Dole co-efficient is an empirical constants determined by solute-solvent interactions.

Results and discussion:-
Using the observed values of ultrasonic velocity, viscosity and density, thermodynamical parameters such as internal pressure, free volume, change in internal pressure are calculated and their values are tabulated in table (1) for aqueous CTAB (0.2mM, 0.3mM and 0.4mM) with NaCl (0.1M to 0.5M) solutions at 303K, 308K and 313K respectively.

Internal pressure:-
The determination of internal pressure is very important in the study of the thermodynamical properties of liquids. Internal pressure is the fundamental property of liquid which provides an excellent basis for examining the solution phenomena and studying various properties of liquid state. It is a measure of change in internal energy of liquid solution as it undergoes a very small isothermal change. It is also a measure of cohesive (or) binding forces between the solute and solvent molecules. The interaction depends upon the solvent and solute structure. It measures the molecular cohesion and the instantaneous volume derivatives of cohesive energy associated with an isothermal expansion of the solution.

It is observed that the values of internal pressure decreases with increasing concentration of NaCl and also with different concentration of CTAB for 303K and 308K. Internal pressure values decreases with increasing temperature at all concentration of NaCl and also with CTAB. The decrease of internal pressure may be due to the breaking up of hydrogen bond in the solvent medium and contact ion paring may reduce the association between ion and solvent [7] (K.Renuka Devi and S.Geetha, et al, 2015). Addition of NaCl in aqueous CTAB decreases the cohesive forces of the solvent which is the reason for reduction in ion-solvent interaction resulting in lowering of internal pressure at all temperatures and hence it behaves as structure breaker [8] (C.V Suryanarayana, J. Kuppusami, et al, 1981). This is the behaviour of chloride ions in solution. The same behaviour is noted for 0.2, 0.3 and 0.4mM of CTAB solutions at 303K and 308K. The internal pressure of aqueous solutions of CTAB increases with increasing concentration is observed at 313K. The increasing concentration of CTAB produces more number of hydrophilic and hydrophobic parts that will increase the cohesive forces of CTAB towards NaCl and hence internal pressure increases.

The internal pressure decreases with the rise in temperature because when the temperature is increased, there is a tendency for the ions to move away from each other, reducing the possibility for interaction, which may further reduce the cohesive forces and ultimately leads to decrease in internal pressure [9-10]. It is due to the thermal dissociation of some of the solvent molecules from the solvated ions.

Free volume:-
Free volume is the effective volume in which the centre of a molecule can move when all other molecules are held fixed at their mean positions. The free volume of a solute at a particular temperature and pressure depends only on

internal pressure of the liquid in which it is immersed. The weakening of molecular association leads to large free volume available for molecular motion and reverse effect gives rise to smaller free volume.

From the table (1), it is observed that the free volume increases with increasing concentration of surfactant CTAB and also with concentration of NaCl at two temperatures viz., 303K and 308K. Free volume increases with concentration of solute NaCl and decreases with increasing concentration of aqueous CTAB at 313K.

At 313K, when the solute is added to solvent, the structure of solvent is broken. The available space of solvent in the solution is reduced hence the solution becomes more compressed. So the free volume decreases with rise in concentration of CTAB [11] (K.Renuka Devi, A.Gomathiyalini, et al., 2016). The decrease in free volume in the system shows that the strength of interaction decreases gradually with the increase in CTAB concentration. The decrease in free volume is due to the presence of tightly packed solvent molecules around the ions at 313K. This indicates that there is a significant interaction between ions and solvent molecules.

When the temperature rises, the repulsive force between the solute and solvent is more and the free space availability also increases. So, free volume increases with increase in temperature. The increase in free volume and the decrease in internal pressure indicates the existence of strong solute-solvent interaction. Hence, the addition of filler to the surfactant increases the efficiency of CTAB. It is clear from the observations that the cleaning efficiency of surfactant in the presence of NaCl is mainly depends on concentration of CTAB and temperature.

Change in internal pressure:-
Change in internal pressure $(\Delta\pi_i = \pi_i - \pi_0)$ can be positive or negative depending on the solute added. The validity of the relation is tested for the systems studied. Negative $\Delta\pi_i$ denotes that the internal pressure of the solution is lower than that of the solvent. This may be due to the fact that the cohesive forces may get loosened perhaps by breaking hydrogen bonds in water [12] (K.Renuka Devi, S.Rathika et al., 2015). It is observed that the $\Delta\pi_i$ values decrease with increasing concentrations of NaCl and CTAB is noted at all temperatures. It is found by observation that the $\Delta\pi_i$ value is found to be negative for all temperatures and concentration of solution and it reveals that the filler NaCl act as a structure breaker. This may be due to the structure breaking nature NaCl.

Relationship between internal pressure and free volume with concentration:-
The internal pressure and free volume constants A, B, C and D were evaluated by least square method. The values of internal pressure constants A and B are used to confirm the structural behaviour of surfactant molecules. Co-efficient A refers to the attractive component and B to the repulsive component.

In this system, the sign and magnitude of internal pressure B is negative in concurrence with the $\Delta\pi_i$ values. Thus, the effect of repulsive forces or cohesive forces in ion-solvent interactions is very well under stood by $\Delta\pi_i$. B is found to be negative at all concentration of CTAB at all temperatures and hence, $\Delta\pi_i$ is negative indicating that the internal pressure of solution decreases due to the addition of sodium chloride which confirms that NaCl acts as a structure breaker. The free volume of the solution increases with increasing concentration.

The co-efficient A values found to be negative at all concentration of the surfactant solution and also with temperatures. The free volume constants C and D values show the exactly reverse trend as that of A and B in magnitude and sign.

Figure (7 to 10) shows the temperature dependent of A, B, C and D for surfactant solutions studied. A versus temperature curve shows a minimum at 308K for 0.2mM and 0.3mM CTAB. In 0.4mM CTAB, the curve increases with increasing temperature is noted. Variation of B with temperature is shown in fig (9). It is reverse to the variation of A at the all concentration of CTAB. In the case of 0.2mM and 0.3mM CTAB solutions, C values are maximum at 308K. For 0.4mM CTAB, it decreases with increase in temperature. The values of D are reverse as that of C values for all concentration of CTAB. From this observation, it is clear that variation of C is reverse trend to that of A, D is reverse to that of B values.

Relation between viscosity with concentration:-
In order to shed more light on this, the role of viscosity B-coefficient has also been obtained. The values of the B-coefficient represent the solute-solvent interaction and a measure of order or disorder introduced by the solute into the solvent structure [13]. It is also a measure of solute-solvent interaction and the relative size of the solute and

solvent molecules. From the table (2), it is observed that the values of A are positive for all concentration of CTAB and B-coefficients are negative for 0.2mM CTAB and positive for remaining concentration of CTAB except at 0.3mM, where the values are negative at 313K. Since, A is a measure of ionic interaction. It is evident that there is a strong ion-ion interaction in the aqueous CTAB solution is studied, which is indicated by the higher magnitude of A values. The negative value of B is indicative of weak solute-solvent interaction. The magnitude of B clearly confirms that the NaCl is acting as an effective structure-breaker in aqueous CTAB solution at 0.2mM [14] (Sumathi T and Varalakshmi M, et al, 2010). Whereas, the positive values of B is indicative of strong ion-solvent interactions owing to the structure-making tendency of the CTAB molecules.

The temperature dependent of viscosity A and B-coefficients for surfactant solutions are shown in fig (11&12). A versus temperature curves show a minimum at 308K for 0.2mM and 0.3mM CTAB, but in 0.4mM solutions the value of A increases with temperature is noted. Variation of B with temperature is similar to the internal pressure B-coefficient and reverse trend to the viscosity A with temperature.

Table 1:- Values of internal Pressure, free volume and change in internal pressure of aqueous solution of CTAB (0.2mM to 0.4mM) with filler NaCl

Molarity (M)	Internal Pressure (π_i) 10^8 N/m²			Free volume (V_f) 10^{-8} m³			$\Delta\pi_i$		
	303K	308K	313K	303K	308K	313K	303K	308K	313K
0.2mM CTAB with NaCl									
0	25.9477	24.9315	23.9204	2.2446	2.6426	3.1231	0.1055	0.0747	-0.0050
0.1	25.2880	24.3747	23.3400	2.3197	2.7182	3.2184	-0.6597	-0.5567	-0.5803
0.2	24.5203	23.5800	22.5225	2.4036	2.8337	3.3751	-1.4273	-1.3515	-1.3978
0.3	23.6866	22.8432	21.8106	2.5152	2.9347	3.5114	-2.2610	-2.0882	-2.1097
0.4	22.9426	22.1118	21.1732	2.6188	3.0580	3.6413	-3.0050	-2.8196	-2.7471
0.5	22.4320	21.6145	20.6120	2.7023	3.1417	3.7723	-3.5157	-3.3169	-3.3083
0.3mM CTAB with NaCl									
0	25.8965	24.9108	24.0180	2.2608	2.6615	3.1061	0.0543	0.0540	0.0925
0.1	25.2744	24.3653	23.4655	2.3290	2.7280	3.2004	-0.6220	-0.5454	-0.5524
0.2	24.4193	23.5792	22.6574	2.4372	2.8373	3.3500	-1.4771	-1.3315	-1.3605
0.3	23.6289	22.8145	21.9199	2.5422	2.9510	3.4890	-2.2675	-2.0962	-2.0980
0.4	22.8630	22.1011	21.2157	2.6473	3.0688	3.6337	-3.0334	-2.8096	-2.8022
0.5	22.3766	21.5663	20.7158	2.7259	3.1730	3.7475	-3.5198	-3.3444	-3.3021
0.4mM CTAB with NaCl									
0	25.8116	24.8977	24.0502	2.2872	2.6699	3.1017	-0.0305	0.0409	0.1247
0.1	25.2397	24.3474	23.5031	2.3455	2.7399	3.1906	-0.5718	-0.5502	-0.5470
0.2	24.3741	23.5690	22.6915	2.4525	2.8426	3.3357	-1.4375	-1.3286	-1.3586
0.3	23.5699	22.7731	21.9383	2.5670	2.9677	3.4824	-2.2416	-2.1245	-2.1118
0.4	22.7899	22.0502	21.2330	2.6820	3.0911	3.6259	-3.0216	-2.8475	-2.8171
0.5	22.2921	21.5511	20.7808	2.7599	3.1878	3.7260	-3.5194	-3.3465	-3.2693

Table 2:- Values of internal pressure A&B coefficient and free volume C&D coefficient and viscosity A&B coefficient Jones-Dole equation of aqueous CTAB solutions with filler NaCl

Molarity (M)	Temperature (K)	Internal pressure (π_i) N/m²		Free volume (V_f) m³		Viscosity (η) Nsm⁻²	
		Constant A 10^9	Constant B 10^9	Constant C 10^{-8}	Constant D 10^{-8}	Constant A	Constant B
0.2mM	303	-0.1238	-0.6791	0.4675	0.7740	0.1244	-0.0266
	308	-0.2426	-0.5865	0.7251	0.7197	0.1158	-0.0203
	313	-0.1500	-0.6212	0.5676	1.0027	0.1517	-0.0291
0.3mM	303	-0.1836	-0.6606	0.6454	0.6924	0.0977	0.0059
	308	-0.2831	-0.5713	0.8540	0.6539	0.0645	0.0230

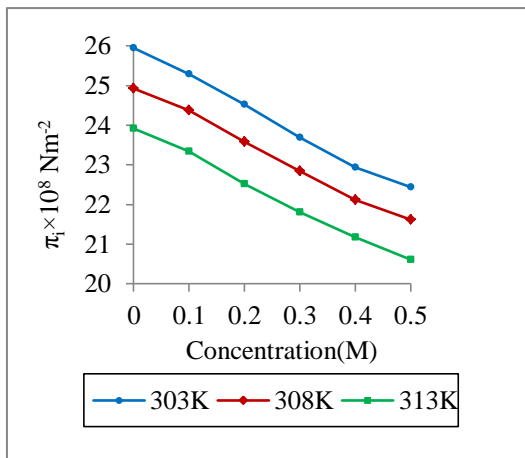|	313	-0.2368	-0.5876	0.7789		0.9745	0.0690	-0.0109
	303	-0.3007	-0.5609	0.8861		0.5890	0.0435	0.0147
0.4mM	308	-0.2853	-0.5751	0.8606		0.6708	0.0667	0.0079
	313	-0.2385		-0.5861	0.8589	0.9197	0.0759	0.0051

Fig1:-Variation of internal pressure of NaCl with
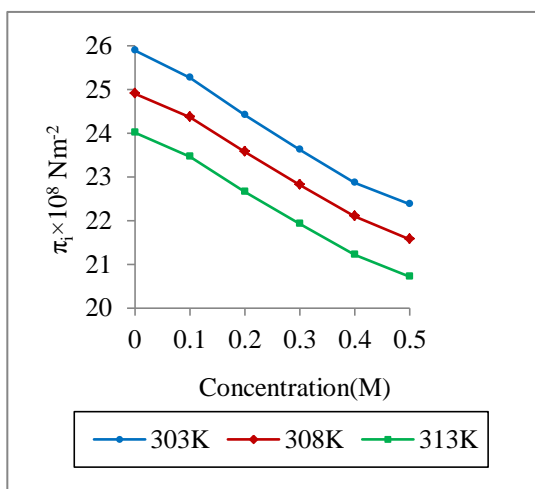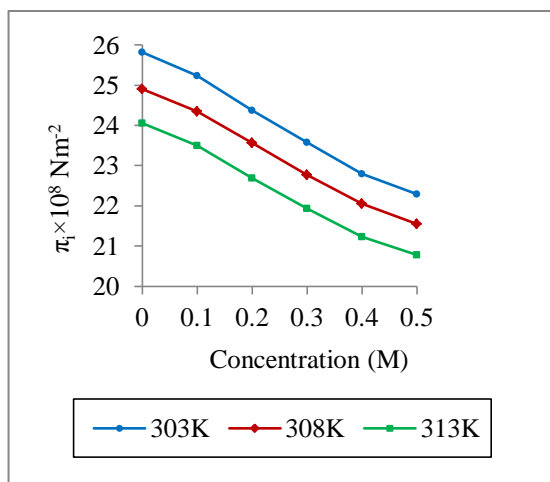0.2mM CTAB at different temperatures
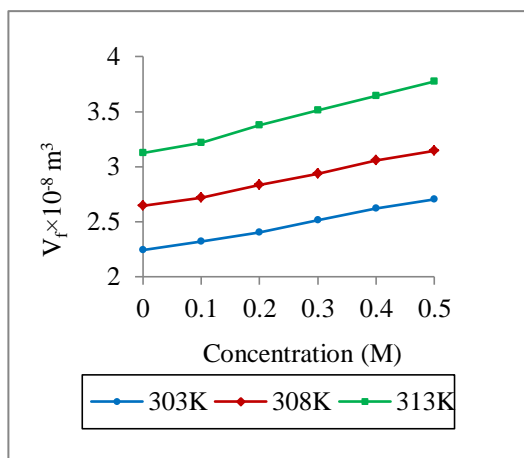
Fig 4:- Variation of free volume of NaCl with
0.2mM CTAB at different temperatures

Fig 2:- Variation of internal pressure of NaCl with
0.3mM CTAB at different temperatures
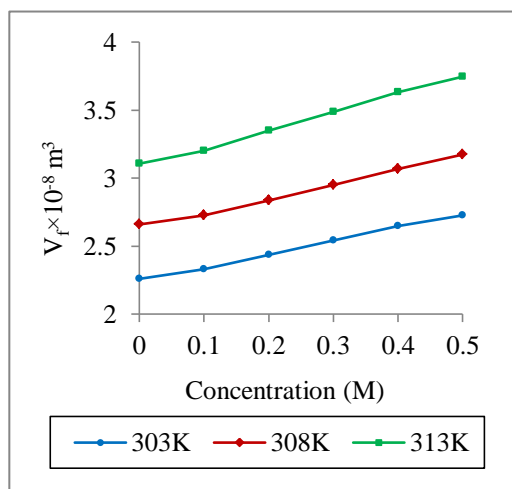
Fig 5:- Variation of free volume of NaCl with
0.3mM CTAB at different temperatures

Fig 3:- Variation of internal pressure of NaCl with 0.4mM CTAB at different temperatures
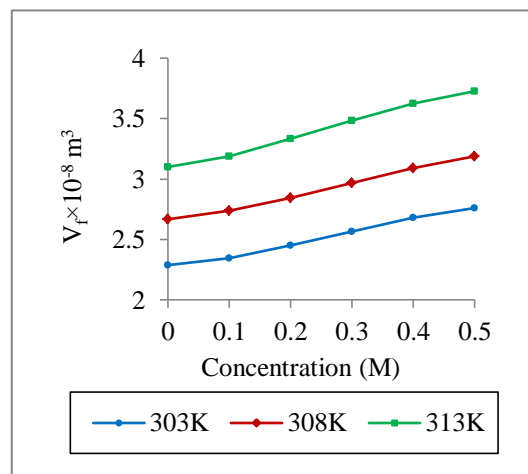
Fig 6:-Variation of free volume of NaCl with 0.4mM CTAB at different temperatures
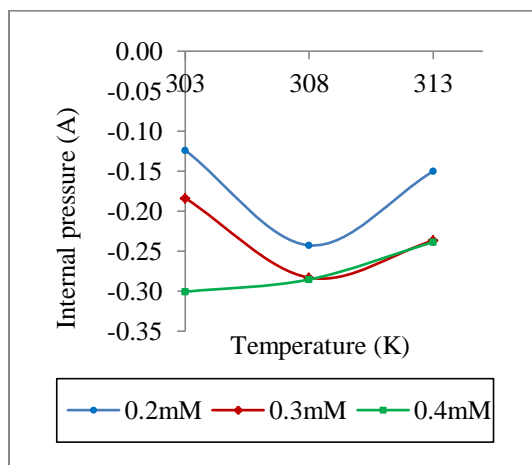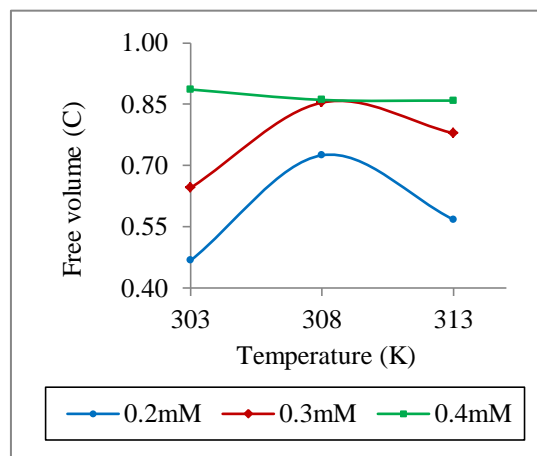

Fig 7:- Variation of A with temperature

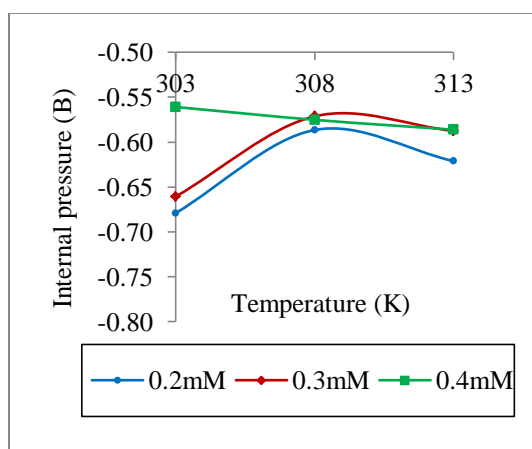**Fig 8:-**Variation of C with temperature

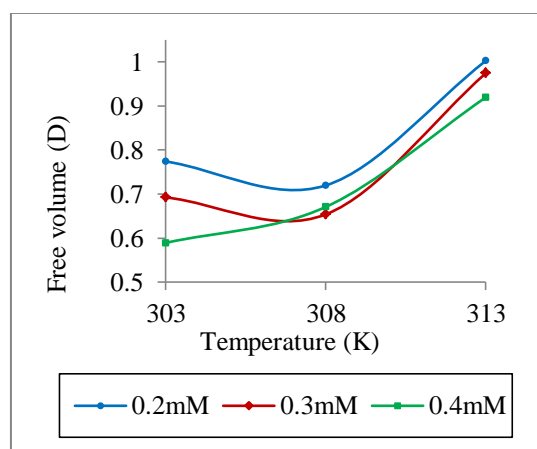**Fig 9:-**Variation of B with temperature

Fig 10:-Variation of D with temperature
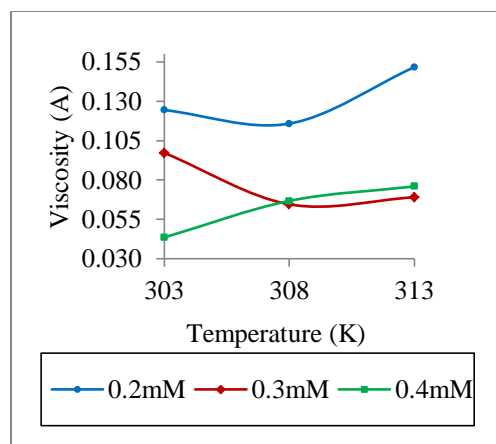
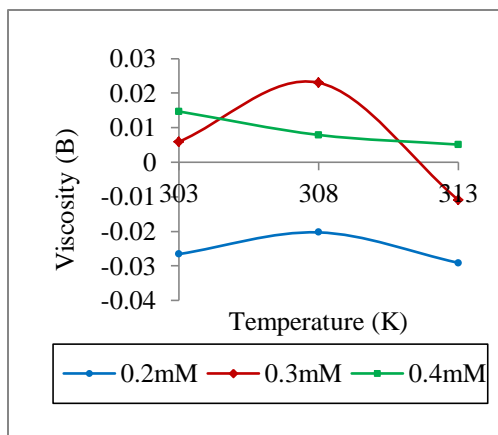**Fig 11:-** Variation of viscosity (A) with tremperatures

Fig 12:- Variation of viscosity (B) with temperatures

Conclusion:-

Ultrasonic investigations of aqueous CTAB with various concentrations of NaCl have been studied. The observed data and variations of thermodynamical parameters with molar concentration of NaCl in aqueous surfactant provide useful information about the nature of intermolecular interactions existing in the solutions. Addition of NaCl in aqueous CTAB decreases the cohesive forces resulting in lowering of internal pressure at all temperatures and hence it behaves as structure breaker. Free volume is an inverse function of π_i. The internal pressure B co-efficient is found to be negative in concurrence with the $\Delta\pi_i$ values. The negative values of B co-efficient confirm the structure breaking nature of NaCl in CTAB. In comparing different concentration of CTAB (0.2mM,0.3mM and 0.4mM), it is found that $\Delta\pi_i$, internal pressure B co-efficient and viscosity B co-efficient are found to be negative. This investigation suggests that the structure-breaking nature of NaCl in the bulk of solvent molecules is noted at lower concentration of 0.2mM CTAB. This leads to the conclusion that NaCl behaves like effective filler at that concentration. It works efficiently and removes strains from clothes.

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