



Ultrasonic and UV Analysis on Aqueous Non-Ionic Surfactants

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ABSTRACT

The evaluation of various acoustical and thermo dynamical parameters which provide an idea into the nature of molecular interactions in aqueous non-ionic surfactant solutions. The measurement of ultrasonic velocity in aqueous solutions an important tool for the calculation of various acoustical parameters. These parameters have been computed through velocity, density and viscosity measurements of non-ionic surfactants (Saponin, Glucocon and Sorbitan sesquioleate) in aqueous medium. This above work was done for different concentration ranges at three different temperatures 303, 313 and 323K using Ultrasonic interferometer. The Critical Micelle Concentration (CMC) was determined to be 1.0% of Water-Saponin, Water - Glucocon, 0.8% of Water - Sorbitan sesquioleate system. These samples were characterised by UV studies.

Keywords: Ultrasonic study, Molecular interactions, Acoustical parameters, Saponin, Glucocon and Sorbitan sesquioleate.

INTRODUCTION

Ultrasonics is a very interesting subject during the recent years¹. To understand the nature and strength of molecular interactions the ultrasonic study of liquids is very important². The study of propagation of ultrasonic waves in liquids and liquid mixtures is extremely abundant helpful for examining the character of inter and intra molecular interactions. Physicochemical properties can be understood among the interfacing parts from ultrasonic velocity estimations and it may be combined with other exploratory information, such as density and viscosity to calculate different acoustical parameters. These are adiabatic compressibility, free length,

acoustic impedance, relaxation time, free volume and internal pressure. This parameter values are important in understanding the molecular interactions in paired blends. Ultrasonic velocity is a vital physical parameter having physical dependency.^{3,4} In recent years studies on acoustic parameters have become an evolving hid^{5,6}. Acoustic parameters are sensitive to changes and are useful in explaining the solute-solvent interaction. Furthermore the ultrasonic velocity measurements have been successfully employed to detect and assess weak and strong molecular interactions⁷.

Surfactants are dispersed in aqueous solution it adsorbs at interface and self-assemble in



bulk solution. Surface active agents also aggregate in solution forming micelles^{8,9}. Physico-chemical studies of surfactant solutions are important from theoretical as well as applied points of view¹⁰. Surfactants are classified either by their use such as soaps, detergents, wetting, foaming agents, corrosion inhibitor or by the structure they are able to build.

In aqueous solution, non-ionic surfactant did not ionise any form of ions and achieving dissolution by hydrogen bonding with water¹¹. The solubility of most of the non-ionic surfactants in water decreases with increasing temperature. Due to their structural features, non-ionic surfactants have different physicochemical properties than from ionic surfactants. Surfactants are to make a significant decrease in surface tension or to reduce the surface tension between two liquids. In aqueous solutions, surfactant molecule start to collective and form micelle in concentration known as Critical Micelle Concentration (CMC) which is one of the most important physical parameters of surfactants.

Saponin is a kind of non-ionic natural surfactant that can be found in many plant species. They are glycosides with high molecular weight¹². The name 'saponin' comes from soap and traditionally used as a natural detergent. Glucopon is a surfactant which is used in laundry and manual dish applications. It shows superior wetting, dispersing and interfacial tension reduction properties. Sorbitan sesquioleate is used in a range of products with skin care products, skin cleansing products, moisturizers, eye makeup and other makeup. In this paper, the effect of non-ionic surfactants (Saponin, Glucopon and Sorbitan sesquioleate) in aqueous medium at various temperatures have been reported. These studies are important in the field of medicinal preparations, agrochemicals and detergents.

MATERIALS AND METHODS

Non-ionic surfactants were obtained from Bio-corporals Chennai, Tamil Nadu, India. The experimental solutions were prepared by adding a known weight of non-ionic surfactants to the distilled water and then stirring under reflux until clear solutions were obtained. Doubled distilled water was used to prepare the stock solution. The ultrasonic velocity measurements in the Saponin, Glucopone and Sorbitan sesquioleate with water were made in the ultrasonic interferometer (model

F81, Mittal Enterprises, New Delhi, India) at a fixed single frequency of 2 MHz and at different temperatures (303, 313 and 323K). The temperature was maintained constant using circulating water from a thermostatically controlled (± 0.1 K) water bath. The values of densities at different temperatures were measured using specific gravity bottle by standard procedure and the viscosity was measured using Ostwald's viscometer with an accuracy of $\pm 0.001\%$ standardized with double distilled water.

Computational aspects of physical parameters

The various physical parameters were calculated by using the standard formulae listed below.

$$\text{Adiabatic compressibility} \quad \beta = 1/U^2 \rho \quad (1)$$

$$\text{The Intermolecular free length} \quad L_f = K_T \beta^{1/2} \quad (2)$$

Where K_T is the Jacobson's constant ($K_T = 2.131 \times 10^{-6}$),

$$\text{Internal pressure} \quad \pi_i = bRT[K \eta/u]^{1/2} \rho^{2/3}/M^{7/6} \quad (3)$$

(Where, b = cubic packing)

T- absolute temperature (K), Where M_{eff} - the effective molecular weight of the mixture¹³.

$$\text{Rao's constant} \quad R_a = (M/\rho)(u)^{1/3} \quad (4)$$

$$\text{Absorption coefficient} \quad \alpha/f^2 = (8\pi^2 \eta / 3\rho u^2) \quad (5)$$

$$\text{Free Volume} \quad V_f = (M_{\text{eff}} u / K \eta)^{3/2} \quad (6)$$

$$\text{Cohesive energy} \quad C_E = V_f \pi_i \quad (7)$$

$$\text{Relaxation time} \quad \tau = 4/3\beta \eta \quad (8)$$

$$\text{Acoustic impedance} \quad za = \rho u \quad (9)$$

$$\text{Solvation number } S_n = M_2/M_1 \left[1 - \left(\frac{\beta}{\beta_0} \right) \right] \left[\frac{100-x}{x} \right] \quad (10)$$

Where M_1 , M_2 are the molecular weight of the solvent and solute, β and β_0 are the adiabatic compressibility of solution and solvent.

RESULTS AND DISCUSSION

The values of Ultrasonic velocity, density and viscosity of aqueous non-ionic surfactants at 303, 313 and 323K are presented in tables 1, 2 and 3. The value of ultrasonic velocity increase with increase of concentration up to Critical Micelle Concentration (CMC) and then it decreases. This indicates the association in the component molecules. This suggests that there is a disruption of water structure occurred due to the addition of non-ionic surfactants. There is a strong association between solute and solvent which is confirmed by

the increase of velocity with increase in concentration and temperature (Fig. 1, 4 and 7). From the study, the CMC of Sorbitan sesquioleate occurs quickly (CMC occurs at 0.8 % concentration) than other two non-ionic surfactants (CMC occurs at 1.0 % concentration). This is because of higher molecular weight of Sorbitan sesquioleate (1175.7 g/mol). The Sugandha. V. and the group stated that when as the temperature will increase, a lot of bonds are broken or a lot of bonds are elongated which ends in dilution of non-ionic surfactants¹⁴. At CMC the velocity is high because the aggregation to form micelles takes place at this concentration¹⁵.

In all the three mixtures, the density and viscosity increases with concentration and decreases with temperature (Tables 1, 2 and 3). When the number of particles increases, the electrostriction and density increases. It is also observed that density for Water – Sorbitan sesquioleate is greater than that for other two systems. To understand the structure and molecular interaction occurred in the solution viscosity is one more main parameter. It is quite higher for Water – sorbitan sesquioleate system than Water – Saponin and Water – Glucocon systems due to strong interaction.

The increase in speed and reduction in compressibility were attributed to formation of chemical element bonds between matter and solvent molecules. The compressibility seems to be decreasing with increasing bond strength shaped by matter and solvent molecules. The increase in ultrasonic velocity (U) and corresponding decrease in adiabatic compressibility (β) with concentration indicate that the molecules are forming a more tightly bound system¹⁶. Fig. 2, 5 and 8 shows the variations of adiabatic compressibility with concentration at various temperatures. The adiabatic compressibility is found to decrease with increase in the concentration of Sorbitan sesquioleate upto 0.8%, Saponin and Glucocon upto 1.0%. Beyond this concentration, when the Sorbitan sesquioleate, Saponin and Glucocon concentration is increased the velocity tends to decrease and adiabatic compressibility is found to increase. This indicate the breaking of water-surfactants beyond the saturation point of 0.8% (Sorbitan sesquioleate), 1.0% (Saponin and Glucocon) and cause the intermolecular free length (L_f) to increase beyond this concentration. The ultrasonic The ultrasonic velocity increases, the intermolecular free length decreases with

Table 1: Ultrasonic velocity and related acoustical parameters in aqueous Saponin solution at different temperatures

Temp K	Conc%	U ms ⁻¹	ρ kgm ⁻³	$\eta \times 10^{-3}$ Nsm ⁻²	$\beta \times 10^{-10}$ N ⁻¹ m ²	L_f Å	$\pi_i \times 10^6$ Pascal	R	$\alpha/f^2 \times 10^{-15}$ Np m ⁻¹ s ²	$V_f \times 10^{-12}$ m ³ mol ⁻¹	Cohesive energy $\times 10^6$	$\tau \times 10^{-12}$ Sec.	za $\times 10^6$ kgm ⁻² s ²	Sn
303	0	1505	998	0.795	4.423	0.419	0.816	0.206	6.144	0.357	0.291	0.468	1.501	-
	0.2	1512	1053	0.826	4.154	0.406	0.084	1.436	5.966	7.57	0.637	0.457	1.592	7434
	0.4	1519	1061	0.842	4.084	0.403	0.049	2.275	5.953	15.8	0.781	0.458	1.611	9933
	0.6	1528	1073	0.873	3.991	0.398	0.038	2.868	5.996	24.1	0.922	0.464	1.639	12085
	0.8	1539	1086	0.892	3.887	0.393	0.032	3.303	5.924	31.6	1.028	0.462	1.671	13954
	1	1545	1098	0.917	3.815	0.389	0.029	3.632	5.954	38.7	1.137	0.466	1.696	14654
	1.2	1534	1109	0.935	3.831	0.39	0.027	3.876	6.14	44.3	1.213	0.477	1.701	13200
313	0	1510	992	0.782	4.421	0.419	0.832	0.207	6.019	0.35	0.291	0.46	1.497	-
	0.2	1517	1041	0.804	4.174	0.407	0.85	1.454	5.816	7.3	0.621	0.447	1.579	6823
	0.4	1525	1050	0.832	4.095	0.403	0.503	2.302	5.874	15.6	0.785	0.454	1.601	9574
	0.6	1533	1061	0.853	4.01	0.399	0.386	2.903	5.867	23.4	0.905	0.456	1.626	11506
	0.8	1544	1069	0.881	3.923	0.395	0.33	3.359	5.886	31.2	1.028	0.46	1.65	12961
	1	1551	1082	0.898	3.841	0.391	0.296	3.691	5.848	37.8	1.12	0.459	1.678	16768
	1.2	1545	1096	0.918	3.822	0.39	0.277	3.931	5.971	43.6	1.207	0.467	1.693	18726
323	0	1515	988	0.687	4.409	0.419	0.801	0.208	5.257	0.29	0.232	0.403	1.496	-
	0.2	1524	1031	0.716	4.176	0.407	0.82	1.47	5.158	6.18	0.507	0.398	1.571	6457
	0.4	1531	1039	0.748	4.106	0.404	0.488	2.33	5.274	13.4	0.653	0.409	1.59	8923
	0.6	1539	1052	0.774	4.013	0.399	0.377	2.932	5.306	20.4	0.768	0.414	1.619	11121
	0.8	1548	1060	0.807	3.936	0.395	0.323	3.391	5.396	27.4	0.887	0.423	1.64	12346
	1	1556	1073	0.835	3.849	0.391	0.293	3.726	5.431	34	0.997	0.428	1.669	16251
	1.2	1550	1085	0.862	3.836	0.39	0.274	3.975	5.609	39.8	1.094	0.44	1.681	17965

Table 2: Ultrasonic velocity and related acoustical parameters in aqueous Glucopon solution at different temperatures

Temp K	Conc%	U ms ⁻¹	ρ kgm ⁻³	η x10 ⁻³ Nsm ⁻²	β X10 ⁻¹⁰ N ⁻¹ m ²	L _r Å	π _r X10 ⁶ Pascal	R	α/f ² X10 ⁻¹⁵ Np m ⁻¹ s ²	V _f X10 ⁻¹² m ³ mol ⁻¹	Cohesive energy X10 ⁻⁶	τ X10 ⁻¹² Sec.	za x10 ⁶ kgm ⁻² s ²	Sn
303	0	1505	998	0.795	4.423	0.419	0.816	0.206	6.144	0.357	0.291	0.468	1.501	-
	0.2	1515	1060	0.834	4.11	0.404	0.076	1.56	5.949	8.8	0.673	0.456	1.605	9447
	0.4	1524	1076	0.856	4.001	0.399	0.041	2.623	5.909	20.519	0.861	0.456	1.639	14457
	0.6	1532	1084	0.879	3.93	0.395	0.03	3.492	5.929	33.337	1.01	0.46	1.66	16958
	0.8	1544	1095	0.891	3.83	0.39	0.024	4.199	5.812	45.899	1.123	0.454	1.69	19763
	1	1540	1107	0.923	3.809	0.389	0.021	4.764	6.002	59.295	1.268	0.468	1.704	19602
	1.2	1537	1118	0.948	3.786	0.388	0.019	5.236	6.14	72.038	1.392	0.478	1.718	19353
313	0	1510	992	0.782	4.421	0.419	0.832	0.207	6.019	0.35	0.291	0.46	1.497	-
	0.2	1521	1049	0.814	4.12	0.405	0.077	1.579	5.798	8.536	0.66	0.447	1.595	9077
	0.4	1534	1063	0.836	3.997	0.398	0.042	2.661	5.728	20	0.847	0.445	1.63	14522
	0.6	1545	1075	0.858	3.897	0.393	0.03	3.531	5.69	32.56	0.997	0.445	1.66	18051
	0.8	1559	1086	0.87	3.788	0.388	0.024	4.247	5.558	44.932	1.111	0.439	1.693	21115
	1	1555	1097	0.893	3.769	0.387	0.021	4.823	5.692	57.254	1.23	0.448	1.705	24955
	1.2	1549	1108	0.924	3.761	0.386	0.019	5.297	5.899	70.134	1.368	0.463	1.716	28079
323	0	1515	988	0.687	4.409	0.419	0.801	0.208	5.257	0.289	0.232	0.403	1.496	-
	0.2	1526	1040	0.724	4.129	0.405	0.074	1.594	5.15	7.196	0.538	0.398	1.587	8481
	0.4	1538	1052	0.756	4.018	0.399	0.041	2.691	5.193	17.266	0.711	0.404	1.617	13432
	0.6	1557	1065	0.789	3.873	0.392	0.03	3.574	5.16	29.047	0.872	0.407	1.658	18508
	0.8	1564	1074	0.816	3.806	0.389	0.024	4.299	5.221	41.011	1.004	0.414	1.679	20172
	1	1560	1086	0.848	3.783	0.388	0.021	4.877	5.407	53.237	1.141	0.427	1.694	24031
	1.2	1555	1098	0.874	3.766	0.387	0.019	5.352	5.566	64.894	1.26	0.438	1.707	27428

Table 3: Ultrasonic velocity and related acoustical parameters in aqueous Sorbitan sesquioleate solution at different temperatures

Temp K	Conc%	U ms ⁻¹	ρ kgm ⁻³	η x10 ⁻³ Nsm ⁻²	β X10 ⁻¹⁰ N ⁻¹ m ²	L _r Å	π _r X10 ⁶ Pascal	R	α/f ² X10 ⁻¹⁵ Np m ⁻¹ s ²	V _f X10 ⁻¹² m ³ mol ⁻¹	Cohesive energy X10 ⁻⁶	τ X10 ⁻¹² Sec.	za x10 ⁶ kgm ⁻² s ²	Sn
303	0	1505	998	0.795	4.423	0.419	0.816	0.206	6.144	0.357	0.291	0.468	1.501	-
	0.2	1514	1036	0.812	4.211	0.409	0.1	1.236	5.938	5.76	0.577	0.455	1.568	4958
	0.4	1521	1049	0.835	4.12	0.405	0.066	1.762	5.947	10.5	0.698	0.458	1.595	6797
	0.6	1526	1053	0.859	4.078	0.402	0.055	2.09	6.035	14.2	0.787	0.466	1.606	6914
	0.8	1531	1061	0.872	4.021	0.4	0.049	2.301	6.021	17	0.846	0.467	1.624	7143
	1	1537	1073	0.894	3.945	0.396	0.046	2.438	6.033	19.7	0.921	0.47	1.649	7576
	1.2	1534	1086	0.917	3.913	0.394	0.045	2.528	6.15	21.97	0.991	0.478	1.665	7272
313	0	1510	992	0.782	4.421	0.419	0.832	0.207	6.019	0.35	0.291	0.46	1.497	-
	0.2	1519	1028	0.801	4.215	0.409	0.102	1.247	5.845	5.67	0.579	0.45	1.561	4799
	0.4	1527	1039	0.827	4.127	0.405	0.068	1.782	5.877	10.4	0.706	0.455	1.586	6597
	0.6	1533	1047	0.845	4.064	0.402	0.056	2.105	5.889	14	0.787	0.457	1.605	7158
	0.8	1538	1055	0.862	4.007	0.399	0.05	2.317	5.904	16.9	0.855	0.46	1.622	7357
	1	1544	1064	0.886	3.942	0.396	0.047	2.463	5.948	19.6	0.933	0.465	1.642	9107
	1.2	1539	1071	0.904	3.942	0.396	0.045	2.566	6.088	21.6	0.988	0.475	1.648	9566
323	0	1515	988	0.687	4.409	0.419	0.801	0.208	5.257	0.29	0.232	0.403	1.496	-
	0.2	1526	1021	0.724	4.205	0.409	0.099	1.257	5.246	4.9	0.488	0.405	1.558	4764
	0.4	1534	1032	0.743	4.117	0.404	0.066	1.797	5.243	8.89	0.588	0.407	1.583	6566
	0.6	1540	1040	0.762	4.054	0.401	0.054	2.123	5.274	12	0.661	0.411	1.601	7132
	0.8	1546	1049	0.789	3.988	0.398	0.049	2.335	5.351	14.9	0.74	0.419	1.621	7496
	1	1551	1055	0.807	3.94	0.396	0.046	2.488	5.39	17.1	0.798	0.423	1.636	8944
	1.2	1546	1064	0.825	3.932	0.395	0.044	2.587	5.517	18.965	0.896	0.432	1.644	9550

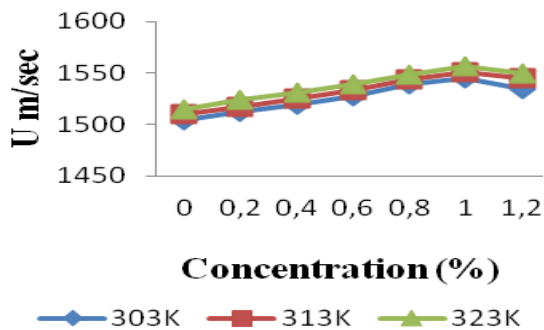


Fig.1. Ultrasonic velocity V_s concentration of Saponin in aqueous solution at different temperatures

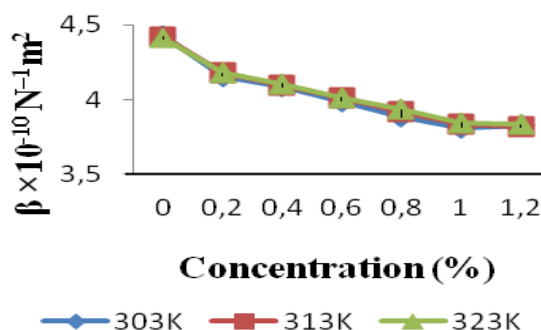


Fig. 2. Adiabatic compressibility V_s concentration of Saponin in aqueous solution at different temperatures

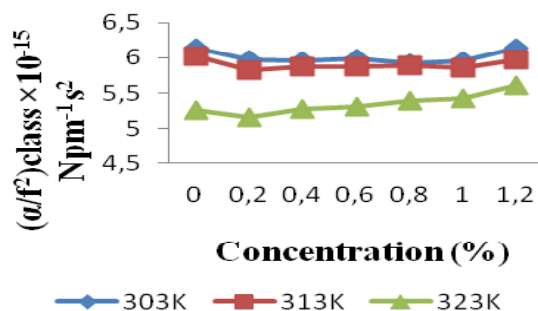


Fig. 3. Absorption co-efficient V_s concentration of Saponin in aqueous solution at different temperatures

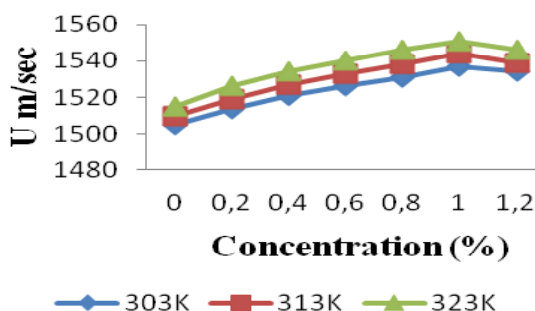


Fig. 4. Ultrasonic velocity V_s concentration of Glucocon in aqueous solution at different temperatures

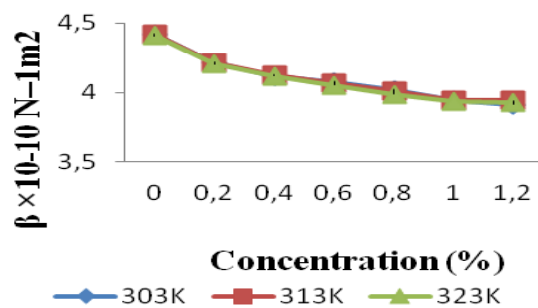


Fig. 5. Adiabatic compressibility V_s concentration of Glucocon in aqueous solution at different temperatures

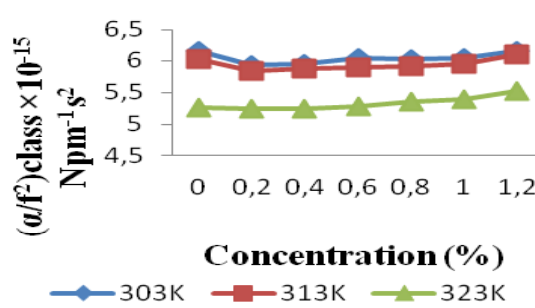


Fig. 6. Absorption co-efficient V_s concentration of Glucocon in aqueous solution at different temperatures

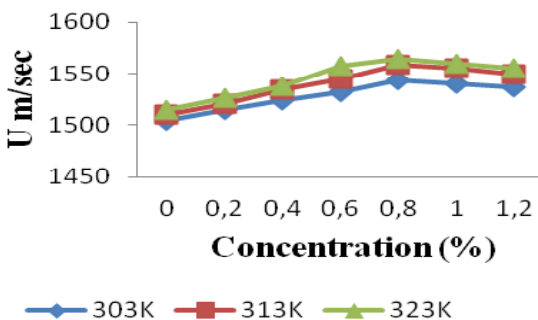


Fig. 7. Ultrasonic velocity V_s concentration of Sorbitan sesquiolate in aqueous solution at different temperatures

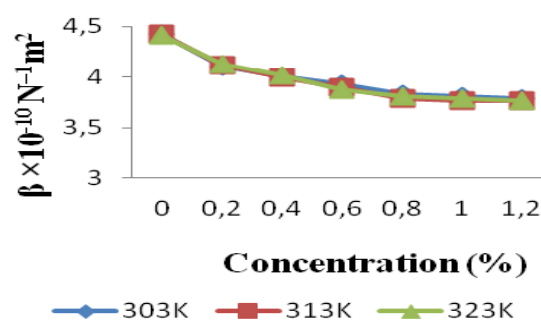


Fig. 8. Adiabatic compressibility V_s concentration of Sorbitan sesquiolate in aqueous solution at different temperatures

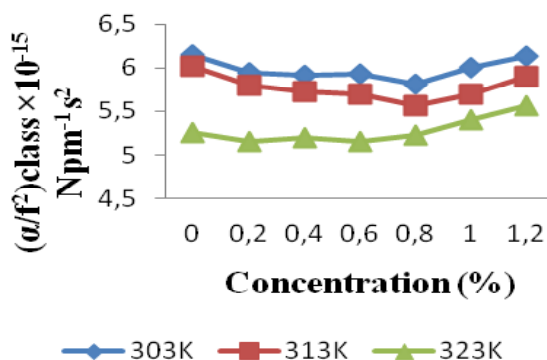


Fig. 9. Absorption co-efficient Vs concentration of Sorbitan sesquioleate in aqueous solution at different temperatures

increase in concentration. This leads to decrease the gap between two molecules which is mentioned by intermolecular free length. This indicates the important interaction between the solute and solvent molecules. When the temperature is increased, there is an increase in free length is occurred¹⁷. It shows that there is an increase of dipole induced dipole attraction occurings in the solution¹⁸.

The nature and strength of forces existing between the molecules the internal pressure decreases with increase of concentration¹⁹.

The non-linear variation of Rao's constant and the gradual increases of acoustic impedance in all the three systems clearly indicate the solute solvent interaction exist in the system but it is dominant in water – Sorbitan sesquioleate system than other two systems.. The absorption Coefficient (α/f^2) of all the three aqueous non-ionic surfactant values are non – linear variations with increase in concentration as shown in Fig. 3, 6 and 9. As the temperature increases the absorption coefficient decreases. This indicates the week interaction between solute and solvent.

Free volume is the average volume in which the centre of molecule can move due to the repulsion of the surrounding molecules. The free volume increases with increases in concentration. The decrease in molecular association causes a rise in free volume. Thus free volume is an inverse function of internal pressure²⁰. However, with the increase of non-ionic surfactant content in water-non-ionic surfactant mixtures, free volume increases. The increase in the concentration of water-non-ionic surfactant mixture, increase of cohesive energy values

are attained and shows that solute-solvent bonding is very strong. The relaxation time, which is in the order of 10-12 sec, is due to structural relaxation process²¹ and in such situation it is suggested that the molecules gets rearranged due to co-operative process²². Further relaxation time decreases with increase in temperature (Tables 1, 2 and 3). With rise in temperature, thermal energy of the system increases causing an increase in excitation energy and hence, falls in values of relaxation time at higher temperature.

Table 4 : UV-Vis absorbance values of Saponin, Glucopone and Sorbitan Sesquioleate

Compounds Name	Concentration ($\times 10^{-3}$) mol dm ⁻³	Absorbance nm
Saponin	0.05	2.45
	0.10	2.51
	0.15	2.81
	0.20	3.01
Glucopon	0.05	2.17
	0.10	2.21
	0.15	2.41
	0.20	2.61
Sorbitan Sesquioleate	0.05	3.6
	0.10	4.04
	0.15	4.42
	0.20	5.08

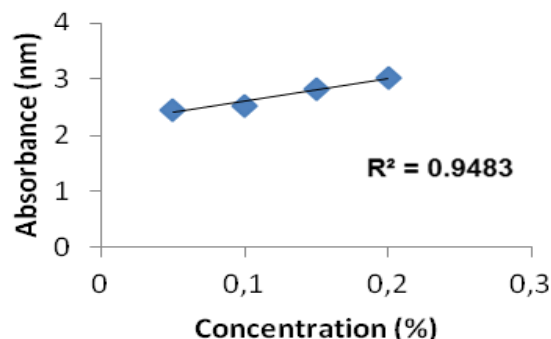


Fig. 10. Lamberts-Beer linear plots for aqueous solution of Saponin at different concentrations

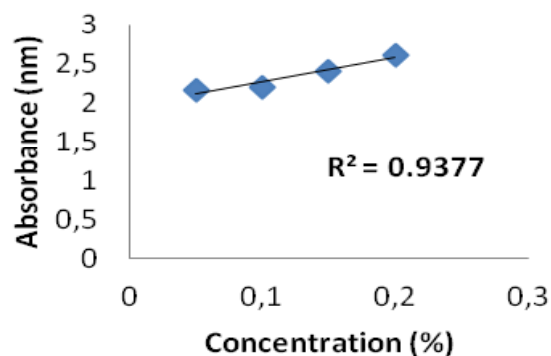


Fig. 11. Lamberts-Beer linear plots for aqueous solution of Glucopone at different concentrations

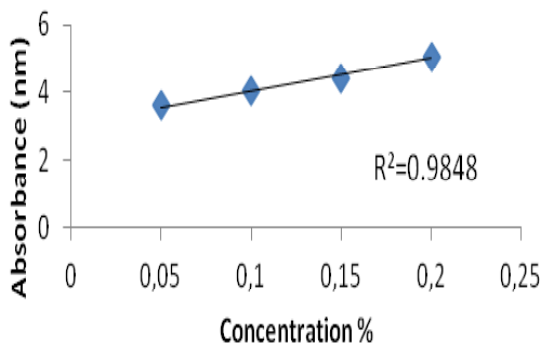


Fig. 12. Lamberts-Beer linear plots for aqueous solution of Sorbitansesquioleate at different concentrations

There is a variation of pressure from particle to particle occurs, when an acoustic wave travels in a medium. To examine specific acoustic impedance in relation to concentration and temperature is important is very important. In this present studies, the acoustic impedance value is increased with increasing concentration of non-ionic surfactant in these solutions. It further supports the possibility of molecular interactions between the water and non-ionic surfactant molecules²³. The structure forming tendency of the non-ionic surfactants are indicated by the positive values of solvation number²⁴. A change in post micellization area exhibited by the values of solvation number, which may be credited to greater consumption of solvent molecules. This reduces the repulsive forces acting between polar heads of ionic micelles²⁵.

UV analysis

UV-Visible spectrum of the aqueous solution of non-ionic surfactants are shown in figures 10 to 12. The spectrum shows a peak with absorbance value increasing with increase in concentration of non-ionic surfactants. A typical Lambert – Beer behaviour has been followed. In all the cases, polarization increases with increase in absorption as shown in Table 4. The

plot concentration versus absorbance is drawn and linear regression analysis has also been carried out as shown in figures 10 to 12. From the absorption study, the mixture of water-Sorbitan sesquioleate has extremely good correlation of absorbance with concentration, $R^2 = 0.9848$ (Fig. 12), but poorer correlation in the mixture of water – Glucopton, $R^2 = 0.9377$ (Fig. 11) and the mixture of water - Saponin, $R^2 = 0.9483$ (Fig. 10). Aqueous mixture of sorbitan sesquioleate has higher polarization power than the other two systems. In all the cases, polarization increases with increase in absorption as shown in Table 4.

CONCLUSION

The linear variation in ultrasonic velocity with increasing concentration suggests the miscibility of non-ionic surfactant with water. Ultrasonic velocity measurement have been extensively applied for assessing the molecular interactions in pure binary liquid mixture. It also determines the elasticity of the medium. Thermo-acoustic parameters can be used to analyze a broad range of molecular processes. Ultrasonic study of non-ionic surfactant is used to determine the intermolecular interactions and different types of forces exist in the medium. This result was confirmed by the UV studies. From the UV results water-sorbitan sesquioleate mixture has high regression value compared to other two mixtures.

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Conflict of Interest

The authors declare that there is no conflict of interests regarding the publication of this article.

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