

Studies of Thermo-acoustical Properties of Polyoxyethylene (20) cetyl ether (Brij-58) in Presence of Additives at Different Temperatures

B. B. Patil*, G. H. Sonawane

Department of Chemistry, KVPS Kisan Arts, Commerce and Science College, Parola, Jalgaon, MS, India.

ABSTRACT

The measurement of ultrasonic velocity and density as a function of temperature and concentration of additives were carried out. The variation of ultrasonic velocity and density of micellar solution of Polyoxyethylene (20) cetyl ether (Brij-58, CMC= 0.0086% w/v) in the presence of polymer PVP and PEO were studied at 298.15, 303.15, 308.15 and 313.15K. Various acoustic parameters such as adiabatic compressibility (β_{ad}), molar volume (V_m), intermolecular free length (L_f), acoustic impedance (Z) and surface tension (γ) of aqueous solution of Brij-58 and Brij-58-polymer mixed solutions were derived from these data. The results were discussed on the basis of polymer-surfactant interactions and hydrophobic interaction, which in turn depends upon the structural arrangement of the linkages involved and difference in the chain which binds the hydrophobic and hydrophilic group in the studied surfactant molecule. It was noted that the ultrasound velocity decreases with increase in temperature. The decrease in the value of β_{ad} and L_f with increase in ultrasonic velocity indicates that there is significant interaction between the surfactant molecule and added polymer PVP and PEO.

Keywords: Nonionic surfactant, PVP, PEO, Ultrasound velocity, Density.

I. INTRODUCTION

Surfactants are the molecules consisting of one water attracting moiety, i.e., hydrophilic (head), and other water repelling or oil attracting moiety, called as hydrophobic (tail). Surfactants and water-soluble polymers are used together in order to boost the properties of the surfactant by the added polymer, and vice versa, or in order to produce properties that none of the surfactant or polymer possesses when used alone. The interactions between surfactant molecules and polymers in aqueous solution are important to many applications such as detergents, personal care products, chemicals, pharmaceutical, mineral processing and petroleum industries [1-2]. The study of the interactions between surfactants and water-soluble polymers in aqueous solutions has long been important because of their numerous industrial applications in pharmaceuticals and biomedicine,

detergents, enhanced oil recovery, and food and mineral processing [3-7].

Polyvinylpyrrolidone (PVP) is a synthetic polymer; consist of linear 1-vinyl-2-pyrrolidone groups. It is a carbon chain polymer which contains amide group in the side substituent and has a poly-N-vinylamide structure. It mostly used for biomedical applications due to its water-soluble, non ionic, non-toxic, and biocompatible nature. It is an amphiphilic polymer and soluble in many non-aqueous solvents. In aqueous solutions, PVP readily forms complexes with different molecules. It has a number of applications in a variety of areas, e.g., as a complexing agent for dyes where it increases the solubility, in aerosol products such as hair sprays, and also a serum for artificial blood preparation [8]. Poly(ethylene oxide) (PEO) is a highly water-soluble polymer, due to its hydrophilic

nature, forms hydrogen bonds with water. It is also a biocompatible polymer.

Fundamentally, conformational changes of polymer chains may occur as a result of polymer surfactant interactions [9]. The addition of polymers to micellar solutions of surfactants may modify micellar properties [10]. Surfactants are often added to polymer solutions to alter the rheological properties and to enhance the stability of dispersions [11-12]. When incorporated into water, surfactants strive to reduce their surface energy by isolating their hydrophobic segments from the aqueous phase [13]. Surfactants are solubilised in water by the hydration of the ether oxygen's of the polyoxyethylene groups. An increase in temperature leads to a decrease in the number of hydrogen bonds, which raises the micellar mass and decreases the CMC. If the temperature continues to increase, the micelle becomes so large and the number of inter micellar interactions increase to such an extent that a sudden onset of turbidity is perceptible even to the naked eye. This temperature is called the cloud point.

Ultrasonic velocity and density of the solution give direct information about molecular interactions of various polymer-solvent systems. The structural and destructural nature, complex formation and association or dissociation of the solvents can be studied. The acoustic parameters give detail information about structural and dynamical properties of polymer-solvent system. When acoustic waves are passed through polymer solution; waves are influenced by the polymer structure and its dynamic processes [14]. Ultrasonic velocity measurements are sensitive to structural changes in surfactant solutions. Micelle formation and stacking can be noticed by this technique [15]. Viscosity measurements at various temperatures and concentrations have been used to characterize containing surfactant as well as surfactant and polymer [16-19].

The variation of ultrasonic velocity with temperature indicates the occurrence of complex formation between unlike molecules through hydrogen bonding (OH-O) [20]. Also it is noted that the ultrasonic velocity decreases with increase in temperature. As the temperature is increased, available thermal energy facilitates the breaking of the bonds between the associated molecules into their monomers. Moreover, increase of thermal energy weakens the molecular forces which tend to decrease the ultrasonic velocity as expected [21]. Intermolecular free length (L_f) shows similar behavior as reflected by adiabatic compressibility. The decreased compressibility brings the molecules to a closer packing resulting into a decrease of inter molecular free length. Intermolecular free length is a predominant factor in determining the variation of ultrasonic velocity in solutions. When inter molecular free length decreases, ultrasonic velocity increases and vice versa, showing an inverse behavior. The decrease in the values of β and L_f with increase in ultrasonic velocity indicates that there is a significant interaction between the surfactant molecule and added polymer, due to which structural arrangement is considerably affected [22].

II. EXPERIMENTAL

2.1 MATERIALS AND METHODS

2.1.1 Ultrasound Velocity

The A.R. grade nonionic surfactant, Polyoxyethylene-20-cetyl ether (Brij-58) (Mole.Wt. 1123.51 g mol⁻¹) was the products of Sigma Aldrich, USA (purity>99%) and uncharged polymer Polyvinylpyrrolidone (PVP) (Mole. Wt. 4000 g mol⁻¹) and Poly ethylene oxide (PEO) (Mole. Wt. 10000 g mol⁻¹) was the product of S. D. Fine Chemical Ltd. and is used as received. Doubly distilled deionized water with specific conductance 2-4 $\mu\text{s cm}^{-1}$ at 303.15 K is used for the preparation of solutions. 0.0086% w/v aqueous solution of Brij-58 was prepared on using distilled water as solvent. The PVP and PEO solutions of 0.005 to 0.05 % w/v were prepared in 0.0086% w/v

Brij-58, which is critical micellar concentration (CMC) of Brij-58. The ultrasonic velocities (U) of surfactant and polymer-surfactant mixtures were measured at 2 MHz using ultrasonic interferometer F-81 (Mittal Enterprises New Delhi). This instrument is connected to fully automatic microprocessor controlled software based instrument having provision to record readings on digital panel and in computer. The test solution in interferometric cell was maintained at required temperature by circulating thermostatic water with an accuracy of ± 0.1 K. The estimated accuracy of sound velocity was ± 0.2 %. The reliability and accuracy of the measurements was checked by obtaining sound velocity data of water and carbon tetrachloride at 298.15K. The ultrasound velocity data were found to be reproducible with in ± 0.5 ms⁻¹ [23].

2.1.2 Density:

Densities (ρ) of the solutions have been determined using bicapillary pycnometer (20 cm³) as described earlier [24, 25]. The pycnometer is filled with experimental liquids and is kept in a water bath. The position of liquid levels in the two arms was noted which could read to 0.01mm. The accuracy of density measurement was ± 0.001 Kg/m³. Three to four measurements were made with average deviation of 0.00005 g cm⁻³. All the measurements were carried out such as to avoid various types of possible degradation of the polymer solution. The speed of sound as well as densities of aqueous solutions of studied surfactant and polymer-surfactant was simultaneously measured at the temperatures 298.15, 303.15, 308.15 and 313.15K.

III. RESULT AND DISCUSSION

The various thermo acoustical parameters are obtained from measured values of ultrasonic velocity (U) and density (ρ) using the standard formulae

$$\text{Adiabatic Compressibility } \beta_{ad} = 1/\rho U^2 \dots(1)$$

$$\text{Intermolecular free length } L_f = K (\beta_{ad})^{1/2} \dots(2)$$

$$\text{Molar Sound Velocity } R_m = (\bar{M}/\rho) U^{1/3} \dots(3)$$

$$\text{Specific Acoustic Impedance } Z = (\rho U) \dots(4)$$

$$\text{Molar Volume } V_m = (\bar{M}/\rho) \dots(5)$$

$$\text{Surface Tension } \gamma = (U^{3/2}) (6.3 \times 10^{-4}) \rho \dots(6)$$

Where U is the ultrasound velocity, ρ is the density; K is the Jacobson's temperature depended constant $K = [(84.875 + 0.375T) \times 10^{-8}]$. \bar{M} is the effective molecular weight and can be calculated using relation.

$$\bar{M} = X_1 M_1 + X_2 M_2 \dots(7)$$

Where M_1 and M_2 are molecular weights and X_1 and X_2 are the mole fractions of component-1 additive and component-2 surfactant solution as solvent [26-33].

The ultrasonic method fails completely, if the velocity of sound in the liquid exceeds 1600 m/s and it is also inferior to thermodynamic method. The estimated accuracy of sound velocity was ± 0.2 %. The reliability of the measurements was checked by obtaining sound velocity data of water carbon tetrachloride and acetone at 298.15 K. The sound velocity data were found to be reproducible with in ± 0.5 ms⁻¹ [34].

3.1.1 Ultrasonic velocity of Brij-58

In the present investigation, the concentration of Brij-58 is taken to be 0.0086% w/v which is CMC of the surfactant. The ultrasonic velocity measurement was made at different temperatures 298.15, 303.15, 308.15 and 313.15K. The thermo acoustical parameters of Brij-58 (0.0086%) at various temperatures are shown in Table.1. The ultrasonic velocity and surface tension of the pure surfactant solution increases with temperature from 298.15K to 303.15K and then decreases up to 313.15K.

Table 1 : Ultrasound velocity and other acoustic parameters of Brij-58 (0.0086 %w/v) at different temperatures.

| Temp K | Density (ρ) kgm ⁻³ | Ultrasonic Velocity (U) ms ⁻¹ | Adiabatic Compre- ssibility (β_{ad})x10 ⁻¹⁰ Kg ⁻¹ ms ² | Intermole- cular Free length (L _f) A ^o | Acoustic Impe- dance (Z)x10 ⁶ kg m ⁻² s ⁻¹ | Molar Volume (V _m)x10 ⁻³ L.mol ⁻¹ | Molar Sound Velocity (R _m)x10 ⁻⁴ mmol ⁻¹ (N/m ^{1/2}) ^{-1/3} | Surface Tension (γ)x10 ⁴ Nm ⁻¹ |
|-----------|--|---|---|---|---|--|--|--|
| 298.15 | 991.6025 | 2136.0 | 2.2103 | 0.2923 | 2.1181 | 160.39 | 2065.65 | 6.167 |
| 303.15 | 991.2410 | 2496.0 | 1.6193 | 0.2526 | 2.4741 | 160.45 | 2176.53 | 7.787 |
| 308.15 | 990.8798 | 2136.0 | 2.2120 | 0.2980 | 2.1165 | 160.51 | 2067.16 | 6.163 |
| 313.15 | 990.1582 | 2008.0 | 2.5048 | 0.3201 | 1.9882 | 160.62 | 2026.49 | 5.613 |

For pure surfactant system ultrasound velocity initially increases as temperature increases, and on further increases in temperature, the ultrasound velocity suddenly decreases, this due the fact that as the temperature increases available thermal energy facilitates the breakings of the bonds between the associated molecules in to their monomer and weakens the molecular forces which tends to decrease the ultrasound velocity [35].

3.1.2 Adiabatic compressibility of Brij-58

Adiabatic compressibility of 0.0086% w/v Brij-58 initially decreases slightly with temperature from 298.15 to 303.15 to obtain minima and then increases up to 313.15K. The minimum compressibility indicates the increases of bond strength and the maximum compressibility indicates the poor bond strength of the molecules. The increases in compressibility may be due to desolvation of molecules of solvent around the ions supporting for weak interactions [36-37].

3.1.3 Surface tension of Brij-58

It has been observed that as temperature increases, surface tension of Brij-58 (0.0086% w/v) increases up to 303.15K and then after decreases up to temperature 313.15K as shown in Table 1.

3.1.4 Ultrasonic velocity, adiabatic compressibility and surface tension of Brij-58-PVP system.

The effect of PVP concentration on Brij-58 at various temperatures is shown in Table 2 and 3. The ultrasonic velocity measurement was made at different temperatures 298.15, 303.15, 308.15 and 313.15K. The ultrasonic velocity and density of 0.0086% Brij-58 at CMC in the presence of PVP having different concentrations and temperatures have been reported in Table 2, and 3. The various acoustic parameters such as adiabatic compressibility (β), inter molecular free length(L_f), specific acoustic impedance (Z), molar sound velocity (R_m), molar volume (V_m) and surface tension (γ) are presented in Table 2 and 3. The speed of sound increases with increase in temperature where as density decreases this may be due the temperature induced conformational changes in polymer-surfactant [38].

Table 2 : Ultrasonic velocity and other acoustic parameters for 0.0086% w/v Brij-58 + PVP at 298.15 and 303.15K

| Conc % (w/v) | Density (ρ) kg m^{-3} | Ultrasonic Velocity (U) ms^{-1} | Adiabatic Compressibility (β_{ad}) $\times 10^{-10} \text{ kg}^{-1} \text{ms}^2$ | Intermolecular Free length (L_f) A° | Acoustic Impedance (Z) $\times 10^6 \text{ kgm}^{-2} \text{s}^{-1}$ | Molar Volume (V_m) $\times 10^{-3} \text{ L.mol}^{-1}$ | Molar Sound Velocity (R_M) $\times 10^{-4} \text{ mmol}^{-1} (\text{N/m}^{1/2})^{-1/3}$ | Surface Tension (γ) $\times 10^4 \text{ Nm}^{-1}$ |
|-----------------|---------------------------------------|--|--|---|---|--|---|--|
| 298.15 K | | | | | | | | |
| 0.005 | 1013.3446 | 2216.0 | 2.0096 | 0.2787 | 2.2456 | 126.66 | 1651.41 | 6.660 |
| 0.01 | 1017.7113 | 2256.0 | 1.9306 | 0.2732 | 2.2960 | 156.28 | 2049.67 | 6.870 |
| 0.02 | 1018.1764 | 2344.0 | 1.7876 | 0.2629 | 2.3866 | 186.35 | 2475.43 | 7.279 |
| 0.03 | 1020.2204 | 2600.0 | 1.4500 | 0.2368 | 2.6526 | 246.14 | 3384.61 | 8.521 |
| 0.04 | 1020.8706 | 2352.0 | 1.7707 | 0.2616 | 2.4011 | 306.10 | 4070.89 | 7.336 |
| 0.05 | 1022.7295 | 2288.0 | 1.8678 | 0.2687 | 2.3400 | 365.56 | 4817.12 | 7.052 |
| 303.15 K | | | | | | | | |
| 0.005 | 1012.4217 | 2400.0 | 1.7148 | 0.2599 | 2.4298 | 126.78 | 1697.46 | 7.499 |
| 0.01 | 1017.1549 | 2432.0 | 1.6622 | 0.2559 | 2.4737 | 156.36 | 2102.79 | 7.686 |
| 0.02 | 1011.3543 | 2608.0 | 1.4537 | 0.2393 | 2.6376 | 187.60 | 2582.38 | 8.486 |
| 0.03 | 1019.6626 | 2664.0 | 1.3819 | 0.2333 | 2.7164 | 246.27 | 3414.02 | 8.833 |
| 0.04 | 1020.1268 | 2496.0 | 1.5735 | 0.2490 | 2.5462 | 306.33 | 4155.35 | 8.014 |
| 0.05 | 1022.1704 | 2448.0 | 1.6325 | 0.2536 | 2.5023 | 365.77 | 4929.59 | 7.800 |

Table: 3 Ultrasonic velocity and other acoustic parameters for 0.0086 % w/v Brij-58 + PVP at 308.15 and 313.15K

| Conc. % (w/v) | Density (ρ) kgm^{-3} | Ultrasonic Velocity (U) ms^{-1} | Adiabatic Compressibility (β_{ad}) $\times 10^{-10} \text{ kg}^{-1} \text{ms}^2$ | Intermolecular Free length (L_f) A° | Acoustic Impedance (Z) $\times 10^6 \text{ kgm}^{-2} \text{s}^{-1}$ | Molar Volume (V_m) $\times 10^{-3} \text{ L.mol}^{-1}$ | Molar Sound Velocity (R_M) $\times 10^{-4} \text{ mmol}^{-1} (\text{N/m}^{1/2})^{-1/3}$ | Surface Tension (γ) $\times 10^4 \text{ Nm}^{-1}$ |
|-----------------|--------------------------------------|--|--|---|---|--|---|--|
| 308.15 K | | | | | | | | |
| 0.005 | 1011.6847 | 2472.0 | 1.6176 | 0.2548 | 2.5009 | 126.87 | 1715.51 | 7.834 |
| 0.01 | 1016.2289 | 2544.0 | 1.5205 | 0.2471 | 2.5853 | 156.50 | 2136.53 | 8.215 |
| 0.02 | 1017.6197 | 2640.0 | 1.4100 | 0.2379 | 2.6865 | 186.45 | 2576.93 | 8.696 |
| 0.03 | 1018.5490 | 2736.0 | 1.3116 | 0.2295 | 2.7868 | 246.54 | 3448.27 | 9.183 |
| 0.04 | 1019.9847 | 2560.0 | 1.4960 | 0.2451 | 2.6112 | 306.37 | 4191.15 | 8.323 |
| 0.05 | 1021.2399 | 2464.0 | 1.6128 | 0.2545 | 2.5163 | 366.10 | 4944.80 | 7.869 |
| 313.15 K | | | | | | | | |
| 0.005 | 1011.3166 | 2464.0 | 1.6287 | 0.2581 | 2.4919 | 126.92 | 1717.28 | 7.793 |
| 0.01 | 1015.3047 | 2472.0 | 1.6118 | 0.2568 | 2.5098 | 156.65 | 2118.11 | 7.862 |
| 0.02 | 1017.4346 | 2576.0 | 1.4812 | 0.2461 | 2.6209 | 186.48 | 2556.41 | 8.380 |

| | | | | | | | | |
|------|-----------|--------|--------|--------|--------|--------|---------|-------|
| 0.03 | 1017.8079 | 2712.0 | 1.3358 | 0.2338 | 2.7603 | 246.72 | 3440.66 | 9.056 |
| 0.04 | 1018.2710 | 2480.0 | 1.5967 | 0.2556 | 2.5253 | 306.89 | 4154.01 | 7.923 |
| 0.05 | 1019.5684 | 2328.0 | 1.8097 | 0.2721 | 2.3736 | 366.70 | 4860.06 | 7.215 |

From the above Table 2 and 3 it is clear that for a given concentration of nonionic surfactant (CMC value) and additive PVP, the ultrasonic velocity, acoustic impedance, molar volume, molar sound velocity and surface tension increases with increase in PVP concentration from 0.01 to 0.03% w/v, then after decreases up to 0.05% w/v. But adiabatic compressibility and intermolecular free length decreases with increase in temperature and polymer concentration. This is due to decreases in density with increases in temperature of Brij-58-PVP solution [39]. The plot of ultrasound velocity vs. concentration of PVP at various temperatures (Fig.1), shows that the maximum interaction exists at 308.15 K. Initially the ultrasound velocity increases as temperature increases from 303.15K to 308.15K and attains a maximum which indicates the strong interaction between the surfactant and polymer. The ultrasonic velocity, acoustic impedance and surface tension were increases up to 0.03% PVP and then decreases with further increase in concentration of PVP, while the adiabatic compressibility and intermolecular free length were decreased with increase in the concentration PVP up to 0.03% (Fig.2) and then increases with further increase in concentration of PVP for all the temperatures studied. The decrease in adiabatic compressibility with increase of concentration of PVP indicates the formation of a large number of tightly bound systems this may be due to a more rigid liquid structure associated with hydrogen bonding of PVP with surfactant such reduction in compressibility has been found in the solution due to solvent molecules [40]. The molar volume and molar sound velocity were increases with increase in concentration of PVP for all the temperatures studied. It has been observed that as concentration of PVP increases surface tension

increase up to 0.03% and then after, it decreases (Fig. 3).

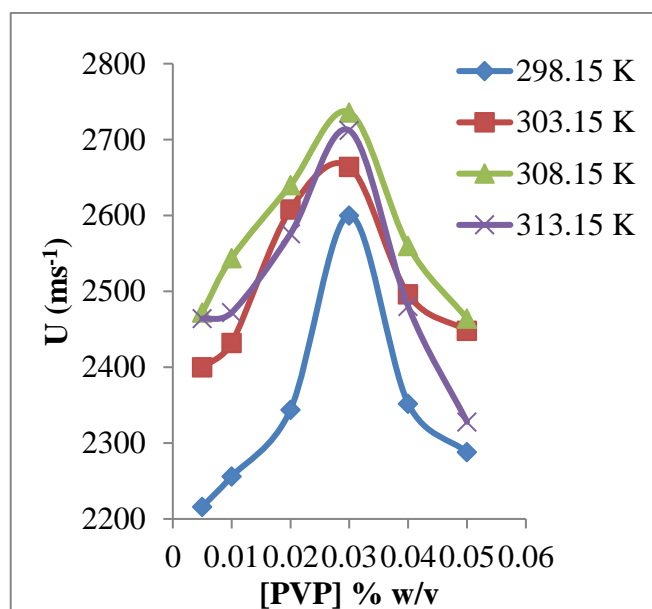


Figure 1. Ultrasonic velocities 0.0086% w/v Brij-58 in presence of PVP at various temperatures and concentrations

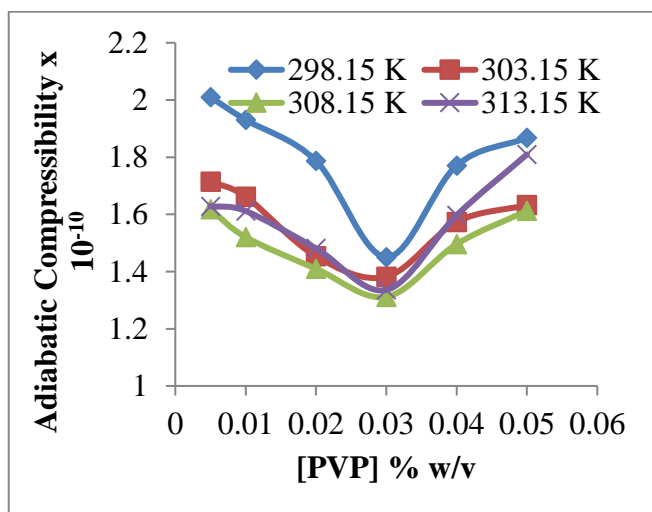


Figure 2. Adiabatic compressibility of 0.0086% w/v Brij-58 in presence of PVP at various temperatures and concentrations

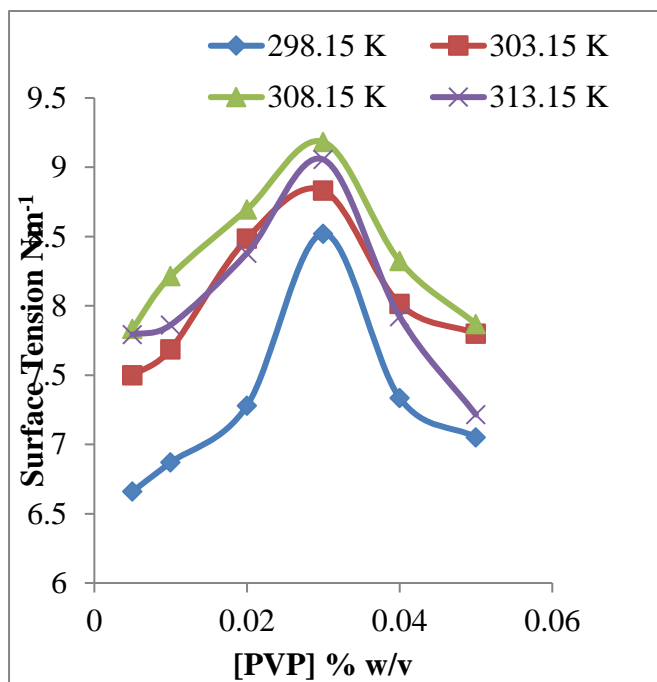


Figure 3. Surface tension of 0.0086% Brij-58 in presence of PVP at various temperatures and concentrations

Also as temperature increases surface tension increases up to 308.15 K and then decreases up to 313.15K. The variation of ultrasonic velocity with temperature indicates the occurrence of complex formation between unlike nuclei through hydrogen bonding (OH-O). Also it is noted that the ultrasonic velocity decreases with increase in temperature because, available thermal energy facilitates the breaking of the bonds between the associated molecules in to their monomers. Moreover increase of temperature weakens the molecular forces which tend to decrease the ultrasound velocity as expected. Intermolecular free length L_f shows similar behavior

as shown by adiabatic compressibility. The decreased compressibility brings the molecules to a closer packing resulting in to a decrease of intermolecular free length, L_f . Inter molecular free length is a predominant factor in determining the variation of ultrasonic velocity in solutions. When intermolecular free length decreases, ultrasonic velocity increases or vice a versa. The interdependence of intermolecular free length and ultrasonic velocity has evolved from a model for sound propagation [41]. The decrease in value of adiabatic compressibility and intermolecular free length with increase in ultrasonic velocity indicates that there is a significant interaction between the polymer and surfactant molecule due to which structural arrangement is considerably affected [42].

3.1.5 Ultrasonic velocity, adiabatic compressibility and surface tension of Brij-58-PEO system.

The ultrasonic velocity and density Brij-58 (0.0086 % w/v) in the presence of PEO having different concentrations 0.005-0.05% and temperatures have been reported in table 4 and 5. The variation of ultrasonic velocity of micellar solution of Brij-58 with concentration of PEO at 298.15, 303.15, 308.15 and 313.15K temperatures is shown in figure 4. The various acoustic parameters such as adiabatic compressibility (β), inter molecular free length (L_f), specific acoustic impedance (Z), molar sound velocity (R_m), molar volume (V_m) and surface tension (γ) are presented in table 4 and 5.

Table 4 : Ultrasonic velocity and other acoustic parameters for 0.0086 % w/v Brij-58+PEO at 298.15 and 303.15K

| Conc. % (w/v) | Density (ρ) kg m^{-3} | Ultrasonic Velocity (U) ms^{-1} | Adiabatic Compressibility (β_{ad}) $\times 10^{-10} \text{ kg}^{-1} \text{ ms}^2$ | Intermolecular Free length (L_f) \AA° | Acoustic Impedance (Z) $\times 10^6 \text{ kg m}^{-2} \text{ s}^{-1}$ | Molar Volume (V_m) $\times 10^{-3} \text{ L.mol}^{-1}$ | Molar Sound Velocity (R_m) $\times 10^{-4} \text{ mmol}^{-1} (\text{N/m}^{1/2})^{-1/3}$ | Surface Tension (γ) $\times 10^4 \text{ Nm}^{-1}$ |
|-----------------|---------------------------------------|--|---|---|---|--|---|--|
| 298.15 K | | | | | | | | |
| 0.005 | 1013.5293 | 2168.0 | 2.0992 | 0.2849 | 2.1973 | 126.64 | 1639.10 | 6.446 |
| 0.01 | 1016.8749 | 2192.0 | 2.0467 | 0.2813 | 2.2290 | 156.40 | 2031.77 | 6.575 |
| 0.02 | 1018.1763 | 2264.0 | 1.9161 | 0.2722 | 2.3052 | 186.35 | 2446.94 | 6.910 |

| | | | | | | | | |
|-----------------|-----------|--------|--------|--------|--------|--------|---------|--------|
| 0.03 | 1019.1981 | 2768.0 | 1.2806 | 0.2225 | 2.8211 | 246.38 | 3459.46 | 9.351 |
| 0.04 | 1019.3840 | 2448.0 | 1.6370 | 0.2516 | 2.4955 | 306.55 | 4131.55 | 7.778 |
| 0.05 | 1020.0343 | 2144.0 | 2.1327 | 0.2871 | 2.1870 | 366.53 | 4726.32 | 6.380 |
| 303.15 K | | | | | | | | |
| 0.005 | 1012.9751 | 2200.0 | 2.0397 | 0.2835 | 2.2285 | 126.71 | 1648.03 | 6.585 |
| 0.01 | 1015.9487 | 2304.0 | 1.8542 | 0.2703 | 2.3407 | 156.55 | 2067.68 | 7.078 |
| 0.02 | 1017.2490 | 2424.0 | 1.6730 | 0.2568 | 2.4658 | 186.52 | 2505.56 | 7.648 |
| 0.03 | 1018.4555 | 3080.0 | 1.0350 | 0.2019 | 3.1368 | 246.56 | 3587.45 | 10.968 |
| 0.04 | 1018.0844 | 2464.0 | 1.6178 | 0.2525 | 2.5086 | 306.94 | 4145.82 | 7.845 |
| 0.05 | 1019.2911 | 2432.0 | 1.6587 | 0.2557 | 2.4789 | 366.80 | 4932.72 | 7.702 |

Table 5 : Ultrasonic velocity and other acoustic parameters for 0.0086 % w/v Brij- 58 + PEO at 308.15 and 313.15 K

| Conc. % (w/v) | Density (ρ) kg m ⁻³ | Ultrasonic Velocity (U) ms ⁻¹ | Adiabatic Compressibility (β _{ad})x10 ⁻¹⁰ kg ⁻¹ ms ² | Intermolecular Free length (L _f) Å | Acoustic Impedance (Z)x10 ⁶ kg m ⁻² s ⁻¹ | Molar Volume (V _m)x10 ⁻³ L.mol ⁻¹ | Molar Sound Velocity (R _M)x10 ⁻⁴ mmol ⁻¹ (N/m ^{1/2}) ^{-1/3} | Surface Tension (γ)x10 ⁴ Nm ⁻¹ |
|-----------------|--------------------------------|--|---|--|---|---|--|--|
| 308.15 K | | | | | | | | |
| 0.005 | 1012.6060 | 2576.0 | 1.4882 | 0.2444 | 2.6085 | 126.76 | 1737.66 | 8.341 |
| 0.01 | 1015.1259 | 2640.0 | 1.4134 | 0.2382 | 2.6799 | 156.67 | 2165.42 | 8.675 |
| 0.02 | 1016.6935 | 2656.0 | 1.3943 | 0.2366 | 2.7003 | 186.62 | 2584.48 | 8.767 |
| 0.03 | 1018.0843 | 3120.0 | 1.0090 | 0.2013 | 3.1764 | 246.65 | 3604.23 | 11.178 |
| 0.04 | 1017.8989 | 2728.0 | 1.3201 | 0.2302 | 2.7768 | 307.00 | 4289.67 | 9.137 |
| 0.05 | 1012.2371 | 2624.0 | 1.4348 | 0.2400 | 2.6561 | 369.35 | 5094.51 | 8.572 |
| 313.15 K | | | | | | | | |
| 0.005 | 1011.5002 | 2304.0 | 1.8624 | 0.2760 | 2.3305 | 126.89 | 1676.04 | 7.047 |
| 0.01 | 1014.4697 | 2352.0 | 1.7819 | 0.2700 | 2.3860 | 156.77 | 2084.98 | 7.290 |
| 0.02 | 1016.1386 | 2416.0 | 1.6860 | 0.2626 | 2.4550 | 186.72 | 2505.53 | 7.602 |
| 0.03 | 1017.1580 | 2944.0 | 1.1343 | 0.2154 | 2.9945 | 246.88 | 3538.36 | 10.236 |
| 0.04 | 1016.9730 | 2464.0 | 1.6196 | 0.2574 | 2.5058 | 307.28 | 4150.35 | 7.836 |
| 0.05 | 1018.1779 | 2424.0 | 1.6715 | 0.2615 | 2.4681 | 367.20 | 4932.69 | 7.655 |

From the above table 4 and 5 it is observed that for (0.0086% w/v) Brij-58-PEO system the ultrasonic velocity, acoustic impedance, molar volume, molar sound velocity and surface tension increases with increase in temperature. But adiabatic compressibility and intermolecular free length decreases with increase in temperature. This is due to decreases in

density with increases in temperature of Brij-58-PEO solution [43].

Variations of ultrasonic velocity of 0.0086% w/v Brij-58 with concentration of PEO at various temperatures are shown in figure 4. It was observed that ultrasonic velocity increases with increase in concentration of PEO in the concentration range of 0.005 to 0.03%.

Ultrasonic velocity is maximum at 0.03% PEO this is due to molecular association of polymer and surfactant. As concentration of PEO increases further from 0.03 to 0.05 % the ultrasonic velocity decreases. The variation of ultrasonic velocity with concentration of PEO is highest at 308.15 K this may be due to structural rearrangement of Bj-58-PEO complex.

The variation of ultrasonic velocity with temperature indicates the occurrence of complex formation between unlike nuclei through hydrogen bonding (OH-O). Also it is noted that the ultrasonic velocity decreases with increase in temperature because, available thermal energy facilitates the breaking of the bonds between the associated molecules in to their monomers. Moreover increase of temperature weakens the molecular forces which tend to decrease the ultrasound velocity as expected [41].

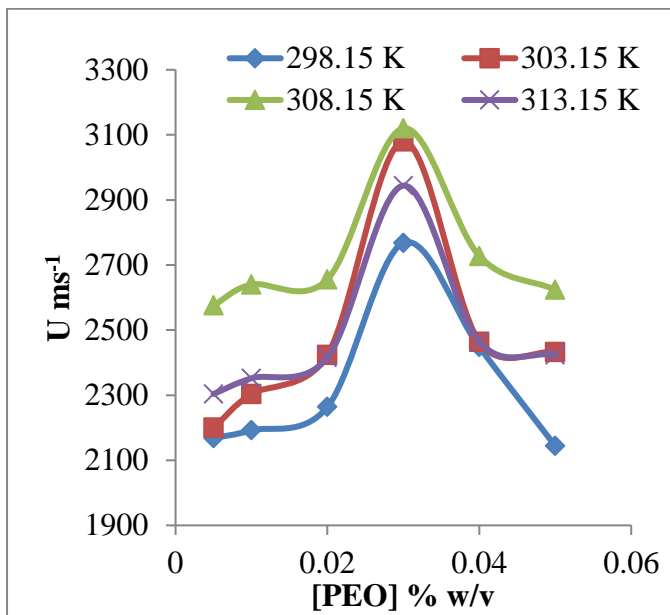


Figure 4. Ultrasonic velocities 0.0086% Brij-58 in presence of PEO at various temperatures and concentrations

The plot of adiabatic compressibility of Brij-97 vs. concentration of PEO at various temperatures is shown in figure 5. It has been observed that as concentration of PEO increases adiabatic compressibility decreases and reaches to minimum at

0.03% PEO, further increase in concentration of PEO adiabatic compressibility increases. Adiabatic compressibility decreases from 298.15 to 308.15K and again increases at 313.15K. The adiabatic compressibility of Brij-58 is less for 0.03% PEO at 308.15K. The decrease in adiabatic compressibility in polymer-surfactant solution is an indication of an increase in intermolecular forces forming aggregates of surfactant molecule around the polymer chain due to which structural arrangement is affected [43].

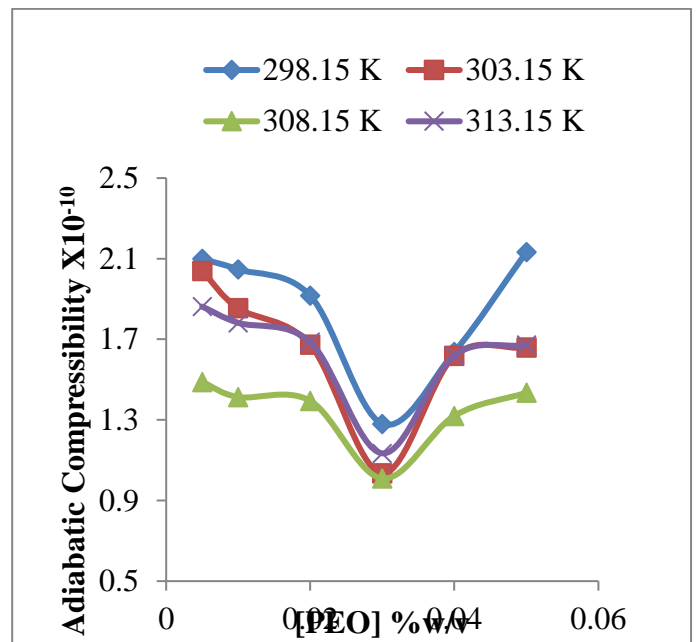


Figure 5. Adiabatic compressibility of 0.0086% Brij-58 in presence of PEO at various temperatures and concentrations

The plot of surface tension of Brij-58 Vs concentration of PEO at various temperatures is shown in figure 6.

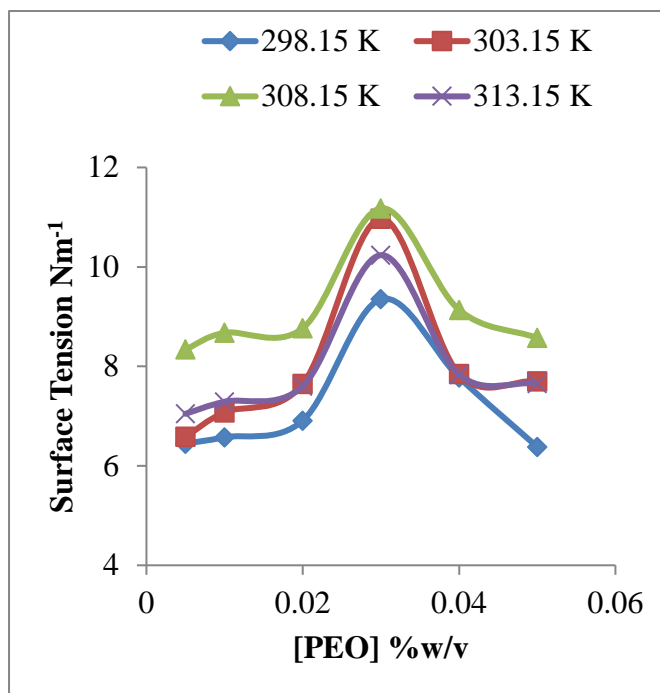


Figure 6. Surface tension of 0.0086% Brij-58 in presence of PEO at various temperatures and concentrations

It has been observed that as concentration of PEO increases surface tension increases up to 0.03% PEO and then after decreases. As temperature increase surface tension increases up to 308.15K for PEO. The surface tension is maximum at 308.15 K but it is higher for 0.02% PEO.

Intermolecular free length (L_f) shows similar behaviour as shown by adiabatic compressibility. The decreased compressibility brings the molecules to a closer packing resulting in to a decrease of intermolecular free length (L_f) Inter molecular free length is a predominant factor in determining the variation of ultrasonic velocity in solutions. When intermolecular free length decreases, ultrasonic velocity increases or vice a versa. The interdependence of intermolecular free length and ultrasonic velocity has evolved from a model for sound propagation [41]. The decrease in value of adiabatic compressibility and intermolecular free length with increase in ultrasonic velocity indicates that there is a significant interaction between the polymer and surfactant molecule due to which

structural arrangement is considerably affected [43,44].

IV. CONCLUSIONS

The ultrasonic velocity data and other acoustical parameters give valuable information to understand the polymer-surfactant interactions in aqueous solutions. The measurement of ultrasonic velocity and other acoustical parameters of aqueous solution of Brij-58 and Brij-58-PVP, and Brij-58-PEO at various temperatures have been carried out.

The trends in acoustical parameters of Brij-58-PVP and Brij-58-PEO systems suggest the stronger interaction between surfactant and polymer. This may be due to the aggregation of surfactant micelles on the polymer chain. Further the variation in acoustical parameters of surfactant alone might be due to the formation of micelle rods in the solution. The decrease in the values of β and L_f with increase in ultrasonic velocity indicates that there is a significant interaction between the surfactant molecule and added polymers, due to which structural arrangement is considerably affected.

V. ACKNOWLEDGEMENT

The authors are thankful to the Principal and Head, Department of Chemistry, KVPS Kisan Arts Commerce and Science College, Parola, Dist. Jalgaon for providing laboratory facilities.

VI. REFERENCES

1. N. Kosaric "Biosurfactants in industry Pure Appl. Chem.", 1992, 64 (11), 1731-1737, doi.org/10.1351/pac199264111731
2. Mohd. Sajid Ali, Goutam Ghosh, Kabir-ud-Din. "Amphiphilic drug persuaded collapse of polyvinylpyrrolidone and poly(ethylene glycol) chains: A dynamic light scattering study",

- Colloids and Surfaces B: Biointerfaces 2010, 75 (2),590-594, doi:10.1016/j.colsurfb.2009.10.002
3. Cahn, A., and Lynn J. *Encyclopedia of Technical Technology*, 1981, 332, Wiley-Interscience, New York.
 4. Goddard and Ananthapadmanaban, "Interactions of Surfactants with Polymers and Proteins", 1993, CRC Press, Boca Raton, FL, 1993, 1-427.
 5. I. De Simone, N. Cocceani, R. Farra, S. M. Fiorentino, G. Grassi, R. Lapasin, D. Hasa, B. Perissutti, M. Grassi, D. Voinovich, "Study on Polymer-Surfactant Interactions for The Improvement of Drug Delivery Systems Wettability", *Chem. Biochem. Eng.* 2012, 26 (4) 405-415.
 6. J.C.T. Kwak, "Polymer-surfactant systems", Dekker, New York, 1998.
 7. A. Avranas, P. Iliou. "Interaction between hydroxypropylmethylcellulose and the anionic surfactants hexane-, octane-, and decanesulfonic acid sodium salts, as studied by dynamic surface tension measurements". *J. of Colloid and Interface Sci.* 2003, 258 (1), 102-109. doi: 10.1016/S0021-9797(02)00129-7
 8. Qi, S., Roser, S., Edler, K.J. et al. "Insights into the Role of Polymer-Surfactant Complexes in Drug Solubilisation/Stabilisation During Drug Release from Solid Dispersions", *Pharm Res* 2013, 30, 290-302. doi.org/10.1007/s11095-012-0873-7.
 9. Kawai, .F. "Microbial degradation of polyethers", *Appl Microbiol Biotechnol* 2002, 58, 30-38, doi: 10.1007/s00253-001-0850-2.
 10. Cabane B. "Structure of some polymer-detergent aggregates in water" *J. Phys. Chem.* 1977, 81, 17, 1639-1645, doi: 10.1021/j100532a008
 11. Philip, J.; Prakash, G. G.; Jaykumar, T.; Kalynasundaram, P.; Mondain Monval, O.; Raj, B. "Interaction between Emulsion Droplets in the Presence of Polymer-Surfactant Complexes", *Langmuir* 2002, 18, 4625-4631, doi: 10.1021/la0256477.
 12. Anis A. Ansari, M. Kamil, Kabir-ud-Din. "Polymer-Surfactant Interactions and the Effect of Tail Size Variation on Micellization Process of Cationic ATAB Surfactants in Aqueous Medium", *Journal of Dispersion Science and Technology* 2013, 34 (5), 722-730. doi: 10.1080/01932691.2012.685850.
 13. O.Nomoto, *J. Phy. Soc. Japan.* 1953, 8, 553.
 14. B.S.Bhadane, T.J.Patil, "Micellization studies on binary mixture of methionine with Polyoxyethylene (10) Cetyl Ether (Brij-56) and Polyoxyethylene (20) Cetyl Ether (Brij-58)", *E-Journal of Chemistry*, 2010, 7(4), 1578-1583. doi: 10.1155/2010/150425
 15. S. Backlund, H. Hoiland, O.J. Kvammen, and E. Ljosland, "An Ultrasonic Study of Sphere to Rod Transitions in Aqueous Solutions of Hexadecyl trimethyl ammonium Bromide", *Acta Chem. Scand.*, 1982 A36, 698-700. doi: 10.3891/acta.chem.scand.36a-0698.
 16. H. Høiland, K. Veggeland, S. Backlund, "Structural Changes in Aqueous Micellar Systems of an Anionic or a Cationic Surfactant", *Surfactants in Solution*. Springer, 1986, 309-316, doi: 10.1007/978-1-4613-1831-6-23
 17. D. Bala Karuna Kumar, K Rayapa Reddy, G Srinivasa Rao, G. V. Rama Rao and C. Rambabu, "Ultrasonic investigation of molecular associations in the binary mixtures of NMP with substituted benzenes at 308.15, 318.15K and atmospheric pressure", *J. Chem. Pharm. Res.*, 2011,3 (5), 274-280,
 18. F. M. Sannaningannavar, B. S. Navati, and N. H. Ayachit, "Studies on thermo-acoustic parameters in the dilute solutions of poly(ethyleneglycol)" *Polymer Bulletin*, 2013, 70, (2), 603-618, doi: 10.1007/s00289-012-0881-0.
 19. G. Zhao, C.C. Khin, and S. B. Chen, "Nonionic Surfactant and Temperature Effects on the Viscosity of Hydrophobically Modified Hydroxyethyl Cellulose Solutions", *J. Phys. Chem. B*, 2005, 109, 14198-14204. doi.org/10.1021/jp051955c.

20. K. Sreekanth, D. S. Kumar, "Study of molecular interactions in the mixtures of secondary alcohols with equimolar mixture of ethanol + formamide from acoustic and thermodynamic parameters" *J. Chem. Pharm. Res.*, 2011, 3(4), 29-41.
21. H. Eyring, J.F. Kincaid, *J. Chem. Phys.*, 1938, 6, 620.
22. Aashees Awasthi, J.P. Shukla, "Ultrasonic and IR study of intermolecular association through hydrogen bonding in ternary liquid mixtures" *J. Mol. Liq.*, 2003, 41, 477, doi: 10.1016/S0041-624X(03)00127-6
23. P. S. Nikam, T. R. Mahale, M. Hasan, "Ultrasonic study of alkanols (C1-C4) in binary mixtures containing ethyl acetate as common component", *Acustica*, 1998, 84(3), 579-584.
24. M. Hasan, U. B. Kadam, A. P. Hiray, A. B. Sawant, "Densities, Viscosities, and Ultrasonic Velocity Studies of Binary Mixtures of Chloroform with Octan-1-ol and Decan-1-ol at (303.15 and 313.15) K", *J. Chem. Eng. Data.*, 2006, 51, 1797-1801, doi.org/10.1021/je060192z
25. P. S. Nikam, R. P. Shewale, A.B. Sawant, M. Hasan, "Limiting Ionic Partial Molar Volumes and Viscosities of Cs⁺, Na⁺, (C₄H₉)₄N⁺, Cl⁻, Br⁻, I⁻, and BPh₄⁻ in Aqueous Acetone at 308.15 K", *J. Chem. Eng. Data.*, 2005, 50, 487-491, doi.org/10.1021/je049698c.
26. Chauhan, S., Singh, R., Sharma, K. and Kumar, K.: "Interaction Study of Anionic Surfactant with Aqueous Non-Ionic Polymers from Conductivity, Density and Speed of Sound Measurements", *J. of Surfactants and Detergents*, 2015, 18, 2, 225-232. doi:10.1007/s11743-014-1613-2.
27. Punitha S. and Uvarani R., "Molecular interactions of surfactants with polymer in aqueous solutions", *J. of Chemical and Pharm. research*, 2012, 4, 387-392.
28. Nithiyantham, S. and Palaniappan, L.: *Arabian Journal of Chemistry*, 2012, 5, (1) 25-30.
29. Bedare, G. R., Bhandakkar, V. D. and Suryavanshi, B. M.: "Ultrasonic Study of Molecular Interactions in Binary Mixtures at 308 K", *Euro. J. Appl. Eng. Sci. Res.*, 2012, 1 (1):1-4.
30. Priya, C. S., Nithya, S., Velraj, G. and Kanappan, A.N., "Molecular interactions studies in liquid mixture using Ultrasonic technique", *Int. J. of Advanced Sci. and Tech.*, 2010, 18, 59-74.
31. Ravichandran, S. and Kumari, C.R.T.: *E-Journal of Chemistry*, 8, 1, 2011, 77- 84.
32. Frindi, M., Michels, B. and Zana, R. "Ultrasonic absorption studies of surfactant exchange between micelles and bulk phase in aqueous micellar solutions of nonionic surfactants with a short alkyl chain. 2. C6E3, C6E5, C8E4, and C8E8" *J. of Phy. Chem.*, 1992, 96(14), 6095-6102. doi: 10.1021/j100193a082.
33. Horiuchi, S. and Winter, G. "CMC determination of nonionic surfactants in protein formulations using ultrasonic resonance technology". *Eur J Pharm Biopharm.* 2015, 92, 8-14. doi: 10.1016/j.ejpb.2015.02.005.
34. P. P. Patil V. R. Shaikh, P. D. Patil, A. U. Borse and K. J. Patil, "Volumetric, isentropic compressibility and viscosity coefficient studies of binary solutions involving amides as a solute in aqueous and CCl₄ solvent systems at 298.15 K", *J Molecular Liquids*, 2018, 264, 223-232, doi:10.1016/j.molliq.2018.05.062.
35. T.J.Patil, "Ultrasonic studies on the micellar behaviour of non-ionic surfactant in aqueous polyelectrolyte at 303 and 313 K", *Asian J. of Chemistry*, 2008, 20(6), 4383-4387.
36. T.J.Patil, H. A. Patil, "Ultrasonic and viscometric studies of the behaviour of cetyltrimethyl ammonium bromide in aqueous polyacrylamide at different temperatures", *Asian Journal of Chemistry*, 2005, 17(3):1979-1983.
37. S.L.Abd-EL-Messigh, *Indian Journal Physics*, 1996, 70B(2), 119.
38. S. Chauhan, M. S. Chauhan, G. S. Chauhan, Sonika, J. Jyoti, "Sound Speed and Density Studies of Interactions Between Cationic Surfactants and Aqueous Gelatin Solution", *Int. J. of*

- Thermophysics, 2012, 33(2), 279-288.
doi:10.1007/s10765-011-1146-0.
39. A. A. Patil, *Chem. Sci. Rev. and Lett.*, 2015, 4(13) 25-30.
40. P. S. Ramesh, D. Gitta, C. Rakkappal, "Ultrasonic studies on aqueous polyethylene oxide in n-alkanols", *J. Mole. Liquids*, 2006, 126, 69-71. doi:10.1016/j.molliq.2005.09.006.
41. S. Velmourougan, J.K.Nambinarayanan, A.S. Rao, B. Krishnan, *Indian J. Phys.* 61B 1987, 105.
42. V.K. Syal, Uma Kumari, Suvarcha Chauhan and M.S. Chauhan, *Indian J. Pure and Appl Phys.*, 1992,30, 719.
43. Rathina K. "Ultrasonic Velocity and Compressibility Variation in Inorganic Sulphates with Aqueous Polymer Solutions" *Int. J. Res. Chem. Env.* 2015, 5(4), 76-79.
44. M. Hasan, U. B. Kadam, A. P. Hiray, A.B. Sawant, "Densities, Viscosities, and Ultrasonic Velocity Studies of Binary Mixtures of Chloroform with Pentan-1-ol, Hexan-1-ol, and Heptan-1-ol at (303.15 and 313.15) K" *J. Chem. Eng. Data.*, 2006, 51, 1797-1801, doi: 10.1021/je0504459.

Cite this Article

B. B. Patil, G. H. Sonawane, "Studies of Thermo-acoustical Properties of Polyoxyethylene (20) cetyl ether (Brij-58) in Presence of Additives at Different Temperatures", *International Journal of Scientific Research in Science, Engineering and Technology (IJSRSET)*, Online ISSN : 2394-4099, Print ISSN : 2395-1990, Volume 6 Issue 3, pp. 377-389, May-June 2019. Available at doi : <https://doi.org/10.32628/IJSRSET207212>
Journal URL : <http://ijsrset.com/IJSRSET207212>