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## Acoustic studies on the binary mixtures of glycerine and water of different dielectric constant, different concentration and at different temperatures

Charles C.Kanakam\*, T.Balakrishnan, K.Tamilselvan

Valliammai Engineering College, S.R.M.Nagar, Kattankulathur, Kancheepuram Dist., Tamil Nadu, (INDIA)

E-mail : charlesckin@yahoo.com

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### ABSTRACT

The solvents and solvent mixtures play a very important role as a medium of carrying out chemical reactions. Often the polarity, the dielectric constant of the solvent and the capacity to take part in intermolecular interaction such as van der Waals interaction, electrostatic attraction and hydrogen bonding of the medium influences the rate of reaction and even the mechanism of the reaction. Solvents like water and glycerol are hydroxylic solvents having high dielectric constant. They are associated even in the pure state. While mixing, intramolecular bonding may give way to intermolecular hydrogen bonding. This leads to nonideal behaviour of the solvent mixtures. This can be qualitatively understood by carrying out ultrasonic studies on the mixture of different composition, at different temperature and at different dielectric constants.

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### KEYWORDS

Intermolecular interaction;  
Ultrasonic parameters;  
Excess functions;  
Non-ideal behavior;  
Dielectric constant.

### INTRODUCTION

Glycerine and water are compounds forming strong intermolecular hydrogen bonding. The network formed by the intermolecular hydrogen bonding in glycerine can be easily broken by water molecules. Hence there can be expected to be a large deviation from the normal behavior of such a binary mixture. This can be easily understood by measuring the density, viscosity, and ultrasonic parameters of binary mixtures of glycerine - water of different proportions. Dielectric constant of different mixtures at different temperatures are measured. A qualitative correlation between the ultrasonic

properties and intermolecular interactions is arrived at from this<sup>[1-4]</sup>. The effect of intermolecular interaction and the factors affecting the dielectric constant can be understood.

The influence of dielectric constant upon the aggregation behavior of biological molecules<sup>[5]</sup> like protein in solution had already been studied taking into account the dielectric constant of mixtures between water, ethanol and glycerol<sup>[2,6-8]</sup>. The use of dielectric constant of solvents in choosing for crystallization, elution chromatography is well documented. It has been reported that protein aggregation takes place at high dielectric constant values, clearly showing the effect of dielectric con-

stant of solvent mixture. The molecular aggregation, association and complexation in solution of binary and ternary mixtures have already been reported<sup>[9-12]</sup>.

With this idea in mind, the ultrasonic behavior of binary mixtures of glycerine and water of different dielectric constant at different concentration and at different temperatures were undertaken.

## EXPERIMENTAL

The density was measured using pycnometer bulk of capacity  $8 \times 10^{-6} \text{ m}^3$  with graduated scale of  $5 \times 10^{-8} \text{ m}^3$  division. The marks of the stem were calibrated using known densities of triple distilled water. The ultrasonic velocities in pure liquids and the binary mixtures are measured using a crystal variable path interferometer 2MHz. The accuracy of densities measurements was 0.001 g/cc while in ultrasonic velocity was found to be  $\pm 0.05\%$ . The viscosity of the liquid mixtures was determined by Oswald's viscometer. The temperature of the test liquids was maintained to an accuracy of  $\pm 0.02^\circ\text{C}$  in an electronic controlled thermostatic water bath.

From the measured density and ultrasonic velocity  $K_s$ ,  $L_f$ ,  $R_A$ ,  $Z$  were calculated the using following relation ship.

Adiabatic compressibility  $\beta = 1/U^2\rho$  ( $10^{-10} \text{ m}^2/\text{N}$ )

Free length  $L_f = K/U\rho^{1/2}$  ( $10^6 \text{ Kg m}^2/\text{s}$ )

Relative association  $R_A = (\rho/\rho_0)(U_0/U)^{1/3}$

Acoustic impedance  $Z = \rho U$

'K' is a temperature dependent constant

$K = (93.875 + 0.375 \times T) \times 10^{-8}$

'T' is the absolute temperature  $\rho_0$ ,  $\rho$ ,  $U_0$ ,  $U$  are the densities and ultrasonic velocities of solvent and solution respectively.

The values of  $\rho$ ,  $U$ ,  $\beta$ ,  $L_f$ ,  $R_A$ ,  $Z$  are shown as function of mole fraction in tables and diagrams.

## DISCUSSION

### Concentration Vs density

The density of binary mixture depends on the densities of the component liquids and their composition. Hence for an ideal solution a linear graph is expected. With in the concentration range studied, the density

depends upon the composition of glycerol-water mixture. Almost a straight-line graph indicating higher density at higher concentration is obtained. Anyhow a straight-line portion is observed between 0.2-0.4% concentrations. Beyond the concentration between 0.4-1.0% a small hump is observed. The increase in density can be explained by the formation of Intermolecular Hydrogen Bonding between solute and solvent molecule. The Intra molecular hydrogen bonding are getting broken in the concentration range of 1-2% and is being replaced by more number of intermolecular hydrogen bonding. Similarly, increase of temperature increases energy of the molecules to increase in volume. This ultimately lowers the density. An ideal binary mixture gives the straight-line graph in both cases. At low concentration (between the 0.5 to 1 %) ideal behavior is noticed. Similarly at high temp of  $45^\circ\text{C}$  almost a straight-line graph is obtained. At all temperatures higher concentration region shows deviation.

### Concentration Vs viscosity

The viscosities of the components and their composition in the mixture determine viscosity of binary liquid mixture. This is true for ideal binary mixture. The system under consideration does not give linear graph. The deviation from ideal behavior is explained on the basis of the breaking up of the intermolecular interaction existing between the pure liquid molecules, formation of intermolecular hydrogen bonding between glycerol/water predominates over disruption of bonds. Further increase in viscosity is attributed to the replacement of intermolecular hydrogen bonding in glycerol, to intermolecular hydrogen bonding. Viscosity depends on the bulk of the molecule in the liquid state and the strength of the intermolecular interaction. For the ideal mixture the viscosity is determined by viscosity of composition and the nature of the components in the mixture. As the concentration increases, viscosity of the mixture is expected to show a rectilinear variation. With the increase of temperature, because of the increase in the kinetic energy of the molecule, the fluidity increases. Thus viscosity is found to decrease with increase in the temperature. Depending on the change in intermolecular interaction with concentration and the temperature, deviations are expected from ideal behavior. The negative deviation for the ideal behavior is noticed. At  $35^\circ$ ,  $40^\circ$

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& 45°C. Positive deviation is noticed at 30°C. The deviations are between 0.8~1.8%. Below 0.8 % mutual dissociation of intermolecular H-bonding takes places leading to increase in volume.

### Concentration Vs ultrasonic velocity

Ultrasonic velocity depends on the density of the medium. Higher the density ultrasonic velocity will be higher. Ultrasonic velocity is inversely proportional to the linear free length and adiabatic compressibility. Whatever factors that affect them  $L_f$  and  $\beta$  will lower the forces of interaction between molecules that determine the magnitude of the U-value.

Initial decrease in U-values can be explained by the disruption of already existing intermolecular attraction with water, by the addition of glycerol from the concentration 0.5% in water with molecular interaction between glycerol and water takes place till the concentration of about 0.8%.

The decrease in U-value indicates disruption of intramolecular hydrogen bonding that exist in glycerol. This takes place between 0.7-1.5% concentrations. This is then replaced by intermolecular hydrogen bonding between glycerol and water up to 1.75% concentration when the U-value is maximum. Further increase in concentration of glycerol brings further disruption of some of the hydrogen bonds existing between glycerol and water. This being slowly replaced by glycerol-glycerol intermolecular interaction. It has been observed that sound wave travels faster in denser medium. Higher the density of the medium, higher is the ultrasonic velocity. Thus, with increase in concentration, U is also expected to increase. Similarly raise of temperature increases the kinetic energy of molecules and an increase of U with temp is expected, though straight lines are expected for ideal solution, nonlinear graphs were obtained. It has been found that U increases from 0.4 to 1.6% and then decreases. A maximum U value is observed at 1.6% concentration. It is interesting to note that maxima is observed for the binary mixture at all the other temperatures for the solution of concentration 1%. On examining the graph it is seen that maxima is almost around 1% concentration at temperature 30°C-40°C. Similarly a sharp increase in U is noticed around 1% concentration even at 30°C, and maxima around 1.5% concentration. The maxima represents a situation where

strong interaction between unlike molecules take place. At 45°C, another increasing trend is noticed around 1.5% concentration. This may correspond to the breaking of intramolecular hydrogen bonding in trihydroxy compounds leading to the formation of glycerol-water bonds.

### Concentration Vs adiabatic compressibility

$\beta$  is inversely proportional to density and U, Z values while directly proportional to  $L_f$  values. It is quite interesting to note, that the  $\beta$  vs Concentration plots are almost the mirror image of the concentration vs U. Initially the disruption of intermolecular interaction in water increases the  $\beta$ . This is replaced by glycerol/water interaction resulting in decrease of  $\beta$  so all the deviation can be explained in a very similar fashion.

Adiabatic compressibility and ultrasonic velocity are inversely proportional to each other while  $\beta$  and  $L_f$  is directly related to each other. It is also related to density of the medium. Normally denser the medium lower the  $\beta$  value. Lower  $\beta$  value indicates strong intermolecular bonding while higher  $\beta$  value indicates weaker intermolecular force or repulsion operating in the medium. For the temperature 35 to 45 °C almost identical plots are obtained. At these temperatures minima is obtained almost at the same concentration of 1%. There is a decreasing trend from 0.4% to 1% and then an increasing trend. For the mixture at 30 °C also there is a slow decrease from 0.4% concentration, followed by a sharp fall in  $\beta$ , from 1% concentration and reach a minimum around the 1.5% and then there is a sharp increase in  $\beta$  value. At low temperature below 1% concentration the rate of formation of intermolecular bonds between the glycerol is slow. The formation of strong intermolecular forces between glycerol water is indicated. At higher temperature, intermolecular bonds between like molecules weakened hence increase in concentration increase the formation of strong intermolecular bonds between unlike molecules. Increase in  $\beta$  value after the minima is explained by the disruption of intra molecular H-bonds in the trihydroxy compound glycerol. At 45°C the above said process give way to the formation of glycerol-water bonds showing further decrease in  $\beta$  value with increase in concentration.

### Concentration Vs acoustic impedance

The  $Z$  is directly proportional to  $U$  and inversely proportional to  $L_f$ ,  $\beta$  and  $RA$ . This fact is very clear from the type of graphs obtained for  $Z$  vs  $C$ ,  $U$  vs  $C$ ,  $L_f$  vs  $\beta$  and  $\beta$  vs  $C$ .

The graph obtained for  $U$  is quite identical to the graph for  $Z$  vs concentration as predicted by the curve. The decrease in  $Z$  values are explained by the disruption of intermolecular bond that exist already and the increase due to the formation of new bonds.

### Concentration vs acoustic impedance

$Z = U\rho$ . This shows that  $Z$  values increase with density or ultrasonic velocity. This is very much clear by comparing the graph obtained for  $Z$  vs  $C$  and  $U$  vs Concentration. Similarly when the former graph is compared to that of  $\beta$  Vs Concentration, the inverse proportionality of  $Z$  and  $\beta$  is clearly seen ( $\beta = 1/Z * \rho * U$ ). The behavior of the mixtures with respect to variation of  $Z$  with temperature is almost the same as that of  $U$  and inverse for that of  $\beta$ .  $\beta$  has higher value for 30 °C while at the same temp  $Z$  &  $U$  values are very low. Increase in  $Z$  is explained by the formation of strong intermolecular forces between unlike molecules while the decrease indicates the rupture of intramolecular H-bonds of glycerol. Maxima appears at 1% concentration for 35°C, to 45°C while for 30°C it is between 1.5 & 2.0%.

### Concentration Vs relative association

The relative association is low at low concentration of glycerol. This is because the addition of solute disrupts the intermolecular bonds mutually.

Relative association is influenced by the two factors.

(i) The breaking up of solvent molecules on addition of solute hence resulting in increase in  $RA$  values.

The increase in  $RA$  value is noticed in the low concentration region up to 0.5%. This indicates that when glycerol is added the intermolecular hydrogen bonding existing in water is disrupted. Beyond that there is a decrease in  $RA$  values, because formation of glycerol/water aggregate is taking place up to 0.8% concentration from the concentration of 0.8% to 1% there is an increase probably, glycerol being trihydric alcohol, intramolecular hydrogen bonding are broken and re-

formed with water molecules. This takes place for the three hydroxyl groups almost in a stepwise fashion. With further increase in concentration of glycerol, water glycerol/water molecular interaction give way to glycerol/water/glycerol interaction. Relative association of the molecules is directly related to density of the solution at low concentration region  $R_A$  decreases with concentration reaching a minimum at 1.0% & then increase at temperature 35°C to 45°C while the trend is opposite at 30°C. The general trend observed for  $\beta$  is the opposite of  $U$  as seen in the case of  $R_A$ . The decrease of  $R_A$  is attributed to water-glycerol-water type of interaction while increase in  $R_A$  attributed to glycerol-water-glycerol interaction. At higher temp  $R_A$  values are lower as thermal energy is capable of disrupting the intermolecular interaction. Maxima  $R_A$  value is noticed for solution of concentration 1.6 to 2.0% at 35°C while for solution of concentration 0.4 to 1.0% at 30°C. Thus, in the low concentration region the association between the like molecule are favored while increase of temperature favor association for more concentration solution.

### Concentration Vs molar volume

Generally molar volume and density are inversely proportional to each other. Graphically at low concentration region there is a sharp increase in molar volume. The increase is not compensated by the decrease in density as seen from the  $\phi$  vs Concentration and density vs Concentration graphs. This clearly shows that mutual disruption of intermolecular bonds between glycerol and water takes place initially. This is replaced by the intermolecular interaction between glycerol and water. Molar volume is inversely proportion to density of the solution. This is seen in graph of density vs temp and  $\phi$  vs temperature. Initially, there is a steady increase in  $\phi$  value with increase in concentration.  $\phi$  Reaches maximum values at 1.0% concentration at all temperature. Beyond the concentration,  $\phi$  values vary in the same way for all temperature.  $\phi$  attains maxima at the high temperature. In a particular temperature,  $\phi$  values increases with concentration. The initial increase in  $\phi$  value is comparatively higher in all cases. For the solution at 30°C, there is an increase in  $\phi$  value with concentration, reaching the maximum at 0.176M solution and then decrease. It has been noticed that the behav-

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ior of the binary mixture at 30°C is anomalous when compared to the other temperature.

### Concentration Vs molecular association

The curves obtained for  $M_A$  vs concentration is quite similar to those obtained for  $U$  vs Concentration,  $Z$  vs Concentration and also  $R_A$  vs concentration. The initial high value of  $M_A$  indicates that pure liquids are associated liquids. Addition of one to the other brings about the disruption of intramolecular bonds. This type of graph is very characteristic of di or trihydric alcohol and water.

### Mole fraction Vs molecular association ( $M_A$ )

Molecular association is the measure of association between unlike molecules. Higher the solute concentration higher will be  $M_A$  values. Similarly, it is inversely proportional to  $R_A$  in the sense that associations between unlike molecules increase as the association between the same molecules decrease. Dissociation of solute or solvents leads to association between solute and solvents molecules. Thus water/water and glycerol/glycerol association give way to water-glycerol-water and or glycerol-water-glycerol association.  $R_A$  decreases with increase in temperature, while  $M_A$  increase with increase in temperature. This can be explained as follows.

As the temp increases the intermolecular forces between water molecules or between glycerol molecules are weakened. This leads to dissociation and formation of intermolecular hydrogen bonds between unlike molecules. As in the other properties, the behavior of the binary mixture at 35 to 45°C are very similar while it is opposite at 30°C. Maximum molecular association occurs around 1.0% concentration at all temperatures. Molecular association values show an increase except for 30°C with concentration of glycerol. While for other temperatures, there is an initial increase and then fall in molecular association values with increase in concentration at low concentration region at temp 35 to 45°C. The association between unlike molecules predominates the dissociation between like molecules decreases. At the same time, in the high concentration range, dissociation between like molecules predominate while the association between unlike molecules increases.

### Concentration Vs free length

Free length is inversely proportional to density,  $U$  and  $Z$  while directly proportional to  $\beta$ . The initial increase in  $L_f$  value indicates that the addition of glycerol to water leads to dissociation of glycerol/glycerol aggregate. This is followed by glycerol/water interaction. Increase with  $L_f$  beyond 0.5% concentration and another at 1% concentration indicates that the intramolecular hydrogen bonding in glycerol are broken giving rise to glycerol/water interaction. Beyond the concentration 1.5% water/glycerol/water interactions are replaced by glycerol/water/glycerol interaction.

Intermolecular free length  $L_f$  is inversely proportional to ultrasonic velocity & density while  $L_f$  &  $\beta$  vary in the same manner with the change in concentration and temperature of the binary mixture.  $L_f = K/(U\rho)^{1/2} = (\beta\rho)^{1/2}$ ; since  $L_f$  is related to the square root of  $U$ ,  $\beta$  &  $\rho$ . The observable deviation in  $L_f$  are correspondingly reduced hence the sharp positive and negative deviations are small when compared to those of  $U$ ,  $\beta$  &  $\rho$ . Anyhow the trend expected on the lines of  $U$  or  $\beta$  is quite clear from the variation of  $L_f$  with concentration & temperature. As seen in other cases the behavior at 30°C is different from those at 35°C, 40°C & 45°C, maxima appears at 1.0% for the latter.

### Molar concentration vs $\beta^E$ (Negative function)

Adiabatic compressibility is a measure of the void or free space available in the solvent structure higher the latter lower is  $\beta$ -value.

The initial decrease in  $\beta^E$  value indicates that in very dilute solution intermolecular hydrogen bonding in the added glycerol molecules are broken. Further  $\beta^E$  approaches  $\beta^{id}$ . Further addition of glycerol increases the non-ideal behavior making  $\beta^{exp}$  less than  $\beta^{ideal}$ , because of glycerol/water bonding.

### Excess function

The positive value of excess function indicates that experimental value is greater than the ideal value. The negative value of excess function indicates that experimental value is less than ideal value. A negative value for  $U^E$  indicates the formation of hydrogen bonding between unlike molecules, here between water and glycerol. The positive values of  $U^E$  indicates the rupture of hydrogen bonding between unlike molecules. Even

weak physical interaction, dispersion forces, dipole-dipole interaction leads to positive  $\beta^E$  &  $U^E$  values. The rupture of associated molecules take place by the addition of solute. This increases  $\beta^E$  &  $U^E$  values. When component molecules do not pack well into the each others structure expansion in volume takes place. This leads to positive values of  $\beta^E$  &  $U^E$  values. Liquid of equal molecular size mix with positive  $\beta^E$  &  $U^E$ .

Formation of hydrogen bonding between unlike molecules and mutual dissociation of component molecules leads to decrease or increase in  $\beta$  &  $L_f$  values respectively. Multi hydroxy alcohol with inter and intra molecular hydrogen bonding, smaller number of –OH groups are available for the component resulting in increase of  $\beta$  &  $L_f$ . Variation of all the excess function with concentration and temperature, following trend is observed in the study of the properties of the binary mixture. The behavior at 30°C is different (opposite trend) for that at higher temperature. Thus the maxima or minima occurs around 1.0% concentration.

### Concentration Vs $L_f^E$ (Negative function)

$L_f^E = L_f^{\text{exp}} - L_f^{\text{ideal}}$  most negative values of  $L_f^E$  indicates  $L_f^{\text{ideal}} > L_f^{\text{exp}}$  indicating stronger intermolecular interaction that already exists This is getting broken leading to lower  $L_f^E$  values. When  $L_f^{\text{exp}}$  approaches  $L_f^{\text{ideal}}$ , that is the  $L_f^E$  decreases. This shows that the dissociation predominates association between unlike molecular.

### Concentration Vs dielectric constant

In the range of the composition of the mixture of glycerol/water the DEC is found to give linear variation with concentration. Increasing the concentration of glycerol in the glycerol/water mixture decreases the DEC.

### Dielectric constant Vs density

General trend observed for the experimental result is that there is an increase in density with decrease in DEC of the binary mixture. Almost rectilinear variation is observed for both 30°C and 45°C, while curves with minima and maxima are obtained for 35 & 40°C. Lower the DEC, higher the density. This indicates that at lower DEC weakening of intermolecular bonds between like molecules take place. This is followed by intermolecular bonds between the unlike molecules.

### Dielectric constant Vs density and viscosity

Mixture of glycerol and water with glycerol concentration varying from 0.3 m to 4.0 m were prepared. Density, Viscosity, Dielectric constant and ultrasonic parameters were measured for each mixture at room temperature. Plot of density and DEC with concentration gives almost rectilinear graph, though slight deviations are observed for density.

Viscosity depends on the size of the molecules in the liquids. In the mixture of glycerol and water, each of the molecules experiences a number of intermolecular interactions leading to solvation increasing the bulk. This affects viscosity of the liquid. This is reflected in all the ultrasonic parameters and excess functions. Dielectric constant of the mixture is a very important and fundamental property. The study of variation of all the properties with DEC of the mixtures show that ultimately change in DEC of the mixtures profoundly affects the behavior of liquid mixtures.

### Dielectric constant Vs relative association

Relative Association is very characteristic of highly polar molecules and molecules having hydroxyl groups such as water and alcohol. Relative Association refers to the association between unlike molecules. Often this refers to intermolecular hydrogen bonding between the solute and solvent molecules. For the system under consideration between unlike molecules the RA values refers to glycerol/water association. As we have seen already from the study of all the ultrasonic functions that at very low concentration mutual dissociation of component molecules takes place i.e. with further increase of concentration intermolecular association (glycerol/water) takes place. Higher the DEC of the mixture, lower the concentration of glycerol. It is seen that for higher DEC values  $R_A$  values are low. As the graph is not linear, the wavy pattern indicates the various stages of association between glycerol and water. Relative association is measure of breaking of solvents molecule aggregates by the addition of solute. This increases the relative association.  $R_A$  increases from low concentration by addition of glycerol, reaches maxima around 1.0 to 1.5 % concentration and then decreases. The decrease in  $R_A$  can be attributed to the solvation of glycerol. This trend is observed for 30°C. For higher temperatures there is an initial decrease in  $R_A$  values with addition of glycerol; a minima is

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reached at 1.0 % conc and beyond this, there is an increase. This can be explained by assuming that at higher temp, the energy needed for the breaking up of solvent aggregates is available and hence solvation of solute takes place at 1.0% concentration. Beyond this, breaking up of intramolecular bonding present in glycerol takes place, resulting in increase of  $R_A$  values. This is observed that higher the temperature lower is the DEC values of the mixture. Lower the DEC value  $R_A$  is higher for the glycerol/water system.

### Dielectric constant Vs free length

The variation of  $L_f$  with dielectric constant of the mixture shows that at higher DEC values the  $L_f$  values are lower. At low concentration and at high DEC of the mixture mutual dissociation of intermolecular interaction takes place. This leads to higher value for  $L_f$ . Because glycerol is a trihydric alcohol. The interaction with water is of several types as indicated by the graph.

### Dielectric constant vs Z, V, $\beta$ , and $R_A$

It is seen from the graphs of V or Z vs Dielectric constant, that within the range of measurement at high dielectric constant value, Z or U values decrease significantly with increase in concentration. This shows that addition of glycerol gives rise to dissociation between the molecules. This behavior is also shown at low concentration by the mixture with high DEC value. Similarly, the behavior at high concentration region is shown by the mixture with low DEC.

This is true for all the ultrasonic parameters we have studied such as adiabatic compressibility and relative association.

### Dielectric constant Vs adiabatic compressibility

There is no direct relationship between  $\beta$  and DEC of the binary mixture. At 30°C, a parabolic curve is obtained and maxima occurs at DEC values of 76.10. The maxima appears for the other temperature at different DEC values. The minimum  $\beta$  value indicates that the mixture becomes almost incompressible. This shows that the intermolecular force becomes insignificant. This is the situation that represents the formation of solvents / solute interaction.

### Dielectric constant Vs acoustic impedance

The acoustic impedance is inversely related to  $\beta$ .

This is clearly visible from the shape of the graph. The DEC vs  $\beta$  and DEC vs Z graphs are almost mirror image of each other. Z increases with DEC values, but the increase is sharp. Maxima is attained at DEC values of 76.10 at 30°C, while maxima for higher temperature occur at higher DEC values. Change of temperature affects both DEC values and Z values. Maxima Z values indicate, formation of cluster water-glycerol-water. This cluster formation takes place at both low & high DEC values of the binary mixture.

### Dielectric constant Vs free length

The variation of  $L_f$  with DEC depends on the temperature. At 30°C, increase of DEC of the mixture increase the  $L_f$  values. While at higher temp a wavy graph is obtained with maxima & minima. The minima for temp 35, 40 & 45°C appears around the concentration of 1.0% glycerin and DEC Values decrease with increase in temp. In the binary mixture of glycerol & water, high DEC corresponds to low percentage of glycerol. In this situation the breaking up of inter molecular bonds between like molecules take place leading to increase in  $L_f$  value.

## CONCLUSION

The binary systems of glycerol and water with varying composition were prepared. The density, viscosity and ultrasonic velocity were measured for each mixture at four different temperatures. The other ultrasonic parameters like  $\beta$ ,  $L_f$ , Z,  $R_A$ ,  $V_m$  and  $M_A$  were also calculated using the standard formulae. In addition the excess function of the said parameters was also calculated. All these variables are plotted against i) Concentration ii) Temperature iii) Dielectric constant of the mixture. The graphs obtained were explained on the basis of inter and intramolecular forces, the breaking and formation of hydrogen bonds.

In the variation of all the properties with concentration a definite change is found to occur in the binary system at the concentration of 1% glycerol. That is either maxima in case of V, Z,  $V_m$  and  $M_A$  or minima in the case of  $\beta$ ,  $L_f$ ,  $R_A$ ,  $\rho$  occurs at concentration of 1%. This is especially true for temperature ranging from 35-45°C. At 30°C a different behavior is observed. Different maxima or minima at a concentration of 1.5 %

are observed at 30°C.

An increase in  $V$ ,  $Z$ ,  $M_A$  or decrease in  $\beta$ ,  $L_f$ ,  $R_A$ , and  $\rho$  are explained on the basis of the predominant function of water – glycerol (solvent/solute) interaction reaching a maximum or minimum values at 1% concentration. Beyond the concentration the decrease in  $V$ ,  $Z$ ,  $M_A$  and increase in  $L_f$ ,  $R_A$ ,  $\beta$ ,  $\rho$  are observed. This is explained by the disruption of intramolecular hydrogen bonding; in the trihydroxy compound glycerol some more hydroxyl group are freed in glycerol. Further increase in  $U$ ,  $Z$  with increasing concentration is explained by the formation of hydrogen bonds between freed –OH group of glycerol-water-glycerol.

The influence as DEC on the behavior of mixtures is well known. Thus for the system under consideration higher the DEC, higher is the value of  $U$ ,  $Z$ ,  $\rho$  or  $R_A$  and lower DEC favours higher value of  $\beta$ ,  $L_f$  and  $M_A$ . The aggregation behavior of molecules in the binary mixture is found to depend on the DEC of the mixture.

As the percentage of glycerol increases in the mixture, the DEC of the mixture decreases. It is seen that as the DEC of the mixture decreases, density is found to increase at all temperatures. But there is rectilinear variation of the other properties with change in DEC. DEC of water is very high (80.37) and is lower for glycerol (41.14). Moreover, through both are hydroxylic liquids, glycerol having low DEC is capable of taking part in strong interaction due to hydrogen bonding than the dipole-dipole interaction. This property that takes predominance over the influence of DEC. It is clearly seen that intermolecular H-Bonding between the water and glycerol plays very important role in deciding the property of the binary mixture unlike DMF-water system or DMSO-water system.

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