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Research Article

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Ultrasonic investigation of molecular interaction in aqueous glycerol and aqueous ethylene glycol solution

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ABSTRACT

The experimental measurements of density (ρ), viscosity (η) and ultrasonic velocity (u) of aqueous glycerol and aqueous ethylene glycol solutions were carried out as functions of concentration at 308.15K. The data of ρ, η and u have been used to evaluate the adiabatic compressibility(β ad), intermolecular free length (Lf), acoustic impedance (Z), relaxation time (τ), rao's constant (RM), wada's constant (W), free volume (Vf), absorption coefficient (α/f2), gibb's free energy (ΔG), relative association (RA) and available volume (Va) to elucidate the molecular association in the mixture. The variation of these parameters with concentration of solute indicates the nature of interaction present in the binary mixture.

Keywords: Ultrasonic velocity, adiabatic compressibility, intermolecular free length, acoustic impedance, molecular association.

INTRODUCTION

The unique feature of sound wave property is that it gives direct and precise information of adiabatic properties. In the basic sciences ultrasonic waves have acquired the status of an important probe for the study of structure and properties of matter. The use of ultrasound is one of the well recognized approaches for the study of molecular interactions in fluids. Ultrasonic velocity measurement provides an important tool to study the liquid state. Ultrasonic and thermodynamic parameters derived from these measurements are extremely used to study the molecular interactions in liquid systems, aqueous solutions and liquid mixtures. Ultrasonic study of liquids is a useful technique for understanding its physico-chemical properties.

Ultrasonic measurements are extensively used to study the molecular interactions in pure liquids, liquid mixtures and ionic interactions in pure liquids, liquid mixtures and ionic interactions in solutions comprising of either single or mixed solutes [1-4]. Derived parameters from ultrasonic speed measurement provide qualitative information regarding the nature and strength of interactions in liquid mixtures [5,6]. The ultrasonic velocity measurements find wide applications in characterizing the physico-chemical behavior of liquid mixtures [7-9] and in the study of molecular interactions. Ultrasonic velocity of a liquid is related to the binding forces between the atoms or the molecules. The accurate measurement of density, viscosity, ultrasonic velocity and hence the derived parameters such as adiabatic compressibility, intermolecular free length, free volume and related parameters will give significant information regarding the state of affairs in a solution.

Ultrasonic study of liquids and liquid mixtures has gained much importance during the last two decades [10-13] in assessing the nature of molecular interactions and investigating the physico- chemical behavior of such systems. Speed of sound itself is highly sensitive to the structure and interactions present in the liquid mixtures as it is fundamentally related to the binding forces between the constituents of the medium [14]. For the qualitative estimation of the molecular interactions in solutions, the ultrasonic velocity approach was first studied by

Lageman [15]. Measurements of ultrasonic speed and density have been used to calculate acoustic and thermodynamic parameters that are found to be very sensitive to molecular interact ions [16,17].

EXPERIMENTAL SECTION

The chemicals used were of analytical grade. Triply distilled water was used for preparation of solutions. A special thermostatic water bath arrangement was made for density, ultrasonic velocity and viscosity measurements, in which temperature variation was maintained within ± 0.01oC. Single crystal interferometer (Mittal Enterprises, New Delhi, Fig. 1) with frequency 6 MHz was used in the present work for measurement of ultrasonic velocities of solutions.

Densities of solutions were measured using specific gravity bottle. These values were accurate up to ± 0.1 kg/m3. Viscosities of the solution were measured by Ostwald's viscometer. The accuracy of viscosity in this method is ±0.001 Nsm^{-2}.

Fig 1

RESULTS AND DISCUSSION

From the observed values the adiabatic compressibility (β_{ad}), intermolecular free length (L_f), acoustic impedance (Z), relaxation time (τ), rao's constant (R_M), wada's constant (W), free volume (V_f), absorption coefficient (α/f^2), gibb's free energy (ΔG), relative association (R_A) and available volume (V_a) were calculated.
Adiabatic compressibility was calculated by using the equation,

$$\beta_{ad} = {}^{1}/_{u^2\rho} \qquad (kg^{-1}ms^{-2}) \qquad (1)$$

Where, u = velocity & ρ = density

Intermolecular free length is determined using the following formula given by Jacobson [18,19]

$$L_f = K_T\ \beta_{ad}^{1/2} \qquad (m) \qquad (2)$$

Acoustic impedance is determined from equation,

$$Z = u \times \rho \qquad (kg\ m^{-2}s^{-1}) \qquad (3)$$

The relaxation time (τ) [20] can be calculated from the relation,

$$\tau = ({}^{4}/_{3})\beta\eta \qquad (s) \qquad (4)$$

Rao's constant is calculated by using following equation,

$$R_M = \left(M_{eff}/\rho \right) u^{1/3} \qquad (m^{10/3} s^{-1/3} mol^{-1}) \qquad (5)$$

Wada's constant is calculated by following equation,

$$W = \left(M_{eff}/\rho \right) \beta_{ad}^{-1/7} \qquad (m^3/mole(N/m^2)^{1/7}) \qquad (6)$$

Free volume is calculated by following equation,

$$V_f = \left(M_{eff} u / K\eta \right)^{3/2} \qquad (m^3) \qquad (7)$$

where Meff is the effective molecular weight, which is expressed as Meff = Σ M=mi xi where, x and m are the mole fraction and molecular weight of the individual component in the mixture respectively. K is the temperature independent constant and its value is 4.28 x 10 9.
Absorption coefficient can be calculated using the relation,

$$\left(\alpha/f^2 \right) = 4\pi^2\tau/2u \qquad (s^2 m^{-1}) \qquad (8)$$

Gibbs free energy is calculated from acoustic relaxation time (τ) as follows,

$$\Delta G = RT \ln \left(kT\tau/h \right) \qquad (J mol^{-1}) \qquad (9)$$

Relative association is a function of ultrasonic velocity and is calculated by the equation,

$$R_A = \rho/\rho_o \left(u_o/u \right)^{1/3} \qquad (10)$$

The available volume is a direct measure of compactness in the liquid and the strength of attraction between the molecules of a liquid or a liquid mixture. It can be calculated from Schaaf's relation,

$$V_a = V_m \left(1 - u/u_\infty \right) \qquad (m^3) \qquad (11)$$

Table 1: Experimental parameters (ρ, *η* and u) for both the systems at 308.15 K

Concentration (c)	**$\rho\times10^3$ /kgm^{-3}**	**$\eta\times10^{-3}$ /$kgm^{-1}s^{-1}$**	**u $\times10^3$ /ms^{-1}**
		Glycerol+water	
1%	0.9962	0.7358	1.5168
2%	0.9989	0.7857	1.5264
3%	1.001	0.8173	1.5312
5%	1.005	0.8606	1.5348
10%	1.0176	0.9220	1.5468
		Ethylene glycol+water	
1%	0.9948	0.7440	1513.2
2%	0.9966	0.7776	1520.4
3%	0.9986	0.8006	1527.6
5%	1.0008	0.8237	1531.2
10%	1.0076	0.8616	1542

The experimentally determined values of density (ρ), viscosity (η) and ultrasonic velocity (u) of two systems at 308.15 K are represented in Table 1. The values of adiabatic compressibility (β_{ad}), free length (L_f), acoustical impedance (z), relaxation time (τ) and rao's constant (R_M) of the above two systems are evaluated and are presented Table 2. Table 3 presents wada's constant (W), free volume (V_f), absorption coefficient (α/f^2), Gibb's free energy (ΔG), relative association (R_A) and available volume (V_a).

Table 2: Derived parameters (β_{ad}, L_f, Z, τ and R_M) for both the systems at 308.15 K

Concentration (c)	$\beta_{ad}\times 10^{-10}$ /$N^{-1}m^2$	$L_f\times10^{-11}$ /m	Z ×10^6 /$Kgm^{-2}s^{-1}$	τ × 10^{-12} /s	$R_M\times10^{-3}$ /$m^{10/3}s^{-1/3}mol^{-1}$
			Glycerol+water		
1%	4.3631	4.3760	1.5110	0.4385	0.2091
2%	4.2968	4.3427	1.5247	0.4501	0.2105
3%	4.2609	4.3245	1.5327	0.4643	0.2118
5%	4.2241	4.3058	1.5425	0.4847	0.2142
10%	4.1073	4.2458	1.5740	0.5049	0.2202
			Ethylene glycol+water		
1%	4.3901	4.3896	1.5053	0.4355	0.2092
2%	4.3407	4.3648	1.5152	0.4500	0.2107
3%	4.2913	4.3399	1.5255	0.4581	0.2121
5%	4.2618	4.3250	1.5324	0.4680	0.2149
10%	4.1739	4.2801	1.5537	0.4795	0.2216

Table 3: Derived parameters (W, V_f, α/f^2, ΔG, R_A, V_a) of the two systems at 308.15 K

Concentration (c)	W ×10^{-3} /m^3/mole$(N/m^2)^{1/7}$	$V_f\times10^{-8}$ /m^3mol^{-1}	$\alpha/f^2\times10^{-15}$ /s^2m^{-1}	ΔG× 10^{-21} /$Jmol^{-1}$	(R_A)	$V_a\times10^{-7}$ /m^3
			Glycerol+water			
1%	0.3955	2.4882	5.7007	4.4008	0.9985	9.4628
2%	0.3982	2.3860	5.8147	4.5118	0.9991	8.4085
3%	0.4007	2.2842	5.9794	4.6439	1.0012	7.9005
5%	0.4055	2.1685	6.2274	4.8268	1.0034	7.5670
10%	0.4174	2.0929	6.4366	5.0005	1.0133	6.3308
			Ethylene glycol+water			
1%	0.3957	2.5285	5.6752	4.3715	0.9979	9.8862
2%	0.3985	2.4091	5.8364	4.5108	0.9981	9.1150
3%	0.4013	2.3478	5.9134	4.5867	0.9985	8.3340
5%	0.4067	2.3077	6.0270	4.6776	0.9999	8.0185
10%	0.4206	2.3061	6.1319	4.7809	1.0044	6.9707

In the present investigation, in all the two liquid systems, viscosity, density and ultrasonic velocity increases with increasing concentrations of solute. The increase of density with increase in concentration of solute suggests a fair strong interact ion between solute and solvent molecules. Also increase in values of viscosity with increase in concentration confirms the increase of cohesive forces because of strong interaction between solute and solvent molecules. The value of adiabatic compressibility (βad) and intermolecular free length (Lf) shows an opposite behavior as compared to the ultrasonic velocity (u). It is chiefly the compressibility that decreases due to structural changes of molecules in the mixture leading to an increase in ultrasonic velocity. In general u and Lf have been reported to vary inversely of each other with the composition of the mixture [21-23] as in the present system. The free length decrease with increasing solute concentration indicates a significant interaction between solute and solvent molecules. It suggests a structure promoting behaviour on the addition of solute. The conductivity may provide information regarding the nature and strength of forces existing between the ions.

Further, an increase in acoustical impedance (Z) and relaxation time (τ) with increase in concentration of the salt is noticed in all the two systems. The behaviour of acoustic impedance becomes accountable for the transmission of ultrasonic waves. The relaxation time which is in the order of 10^{-12} sec is due to structural relaxation process [24] and in such a condition it is suggested that the molecules get rearranged due to co-operative process [22]. The increasing trends of Rao's constant or molar sound velocity and Wada's constant or molar comp ressibility with concentration suggest the availability of more number of components in a given region thus leads to a close packing of the medium and thereby increase the interactions. The values of Wada's constant increase with increasing concentration indicate that there must be tight packing of the medium and hence interaction is increasing. Thus there may be solute-solvent interaction occurring. A decrease in free volume with increase in concentration of the salt is noticed in all the two systems. The decrease in free volume shows that the strength of interaction increases steadily with the increase in solute concentration.

The values of absorption coefficient, Gibb's free energy and relative association listed in the table show increasing trend with concentration whereas the values of available volume decreases with increase in concentration for both the aqueous solutions of Glycerol and Ethylene glycol. The increasing value of Gibb's free energy with concentration shows appreciable interaction between solute and solvent molecules. The absorption coefficient trend and available volume trend confirms the earlier conclusions. Relative association evaluates the extent of association of the component in the mixture. The value of relative association increases with increase in concentration signifying strong interaction. The data is in agreement with their observed ultrasonic velocity and density data.

From figure 2, it is apparent that adiabatic compressibility decreases with increase in concentration for both the systems. It is found that the adiabatic compressibility for aqueous glycerol solution is lesser than that of aqueous ethylene glycol solution. In the figures 3 and 4 are presented the values for the intermolecular free length and free volume for aqueous solutions of glycerol and ethylene glycol versus concentration respectively. The values of intermolecular free length and free volume for aqueous glycerol solutions are lesser than that of aqueous ethylene glycol solutions. As can be seen from figure 5 the variation of relative association versus concentration for both the systems. The values of relative association are higher for aqueous glycerol solutions. Figure 6 depicts the variation of available volume versus concentration for both aqueous glycerol and aqueous ethylene glycol solutions.

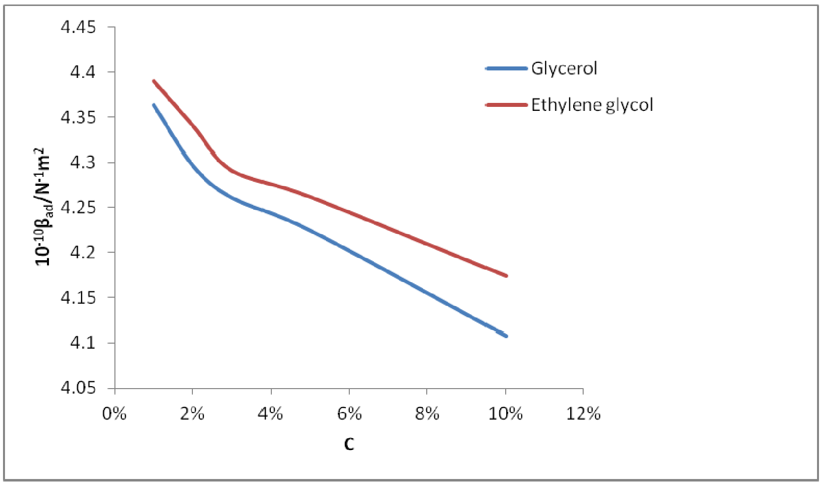

Fig 2

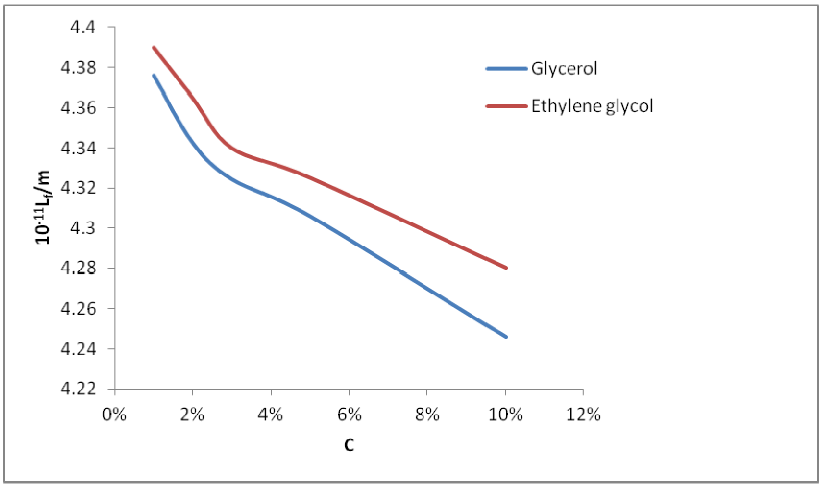

Fig 3

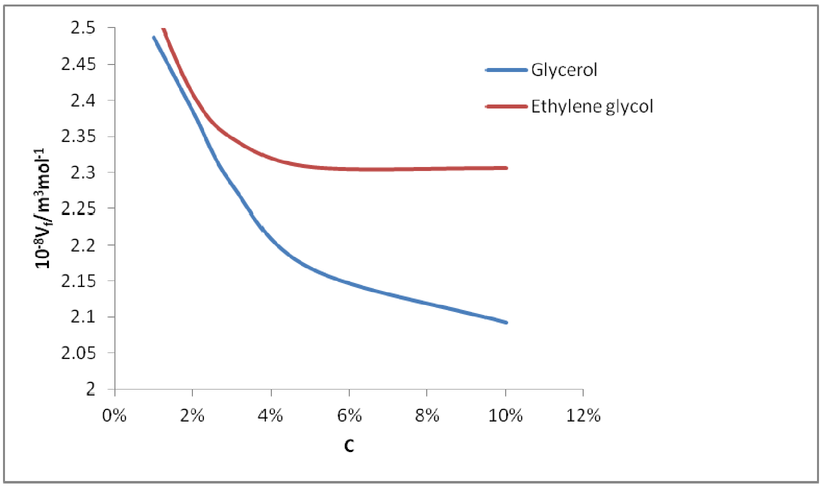

Fig 4

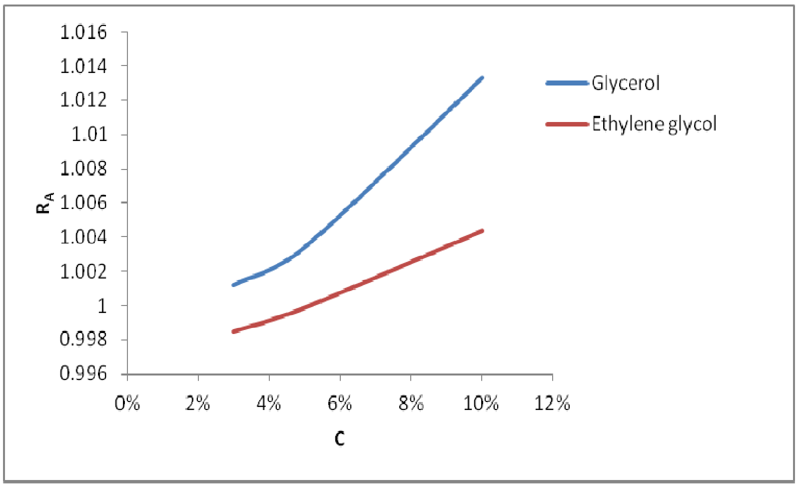

Fig 5

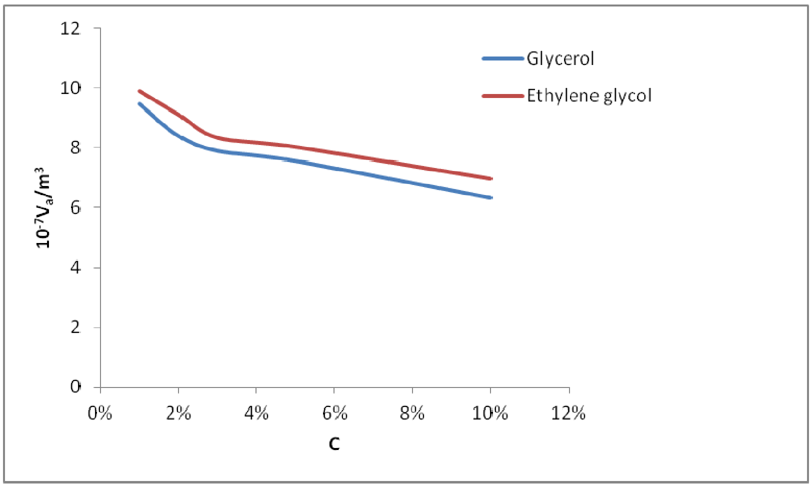

Fig 6

The ultrasonic velocity values and other acoustical properties vary with concentration and these variations indicate a greater association of the molecules. The increase in the ultrasonic velocity in any solution usually indicates a greater association of the molecules in them. The greater association is due to Hydrogen bonding between solute and solvent molecules. A greater cohesion in the solution is introduced as water molecules are attached to the ions strongly by Hydrogen bonding.

CONCLUSION

A systematic study of glycerol and ethylene glycol in water has been carried out at different concentrations using ultrasonic experiments. From ultrasonic velocity and related acoustical parameter values for the binary liquid mixtures of glycerol and ethylene glycol in water at 308.15K, it is concluded that there is a formation of hydrogen bonding between glycerol and water molecules and ethylene glycol and water molecules. The evaluated values clearly confirm th at that the molecular interaction is more pronounced in glycerol-water system comparing to the ethylene glycol-water system. This is due to the greater association between solute–solvent molecules in aqueous glycerol and aqueous ethylene glycol solutions because of the presence of three-OH groups in a glycerol molecule and two-OH groups in ethylene glycol molecule. Hence, it is very obvious that there exists a strong molecular association between the component molecules in the mixtures.

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