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Ultrasonic Investigation of Molecular Interaction in Binary Liquid Mixture of Polyethylene Glycol with Ethanol

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***Abstract*—**Polyethylene glycol (PEG) is a condensation polymer of ethylene oxide and water. It is soluble in water and in many organic solvents. PEG is used to make emulsifying agents, detergents, soaps, plasticizers, ointments etc. Ethanol (C_2H_5OH) also known as ethyl alcohol is a well-known organic compound and has wide applications in chemical industry as it is used as a solvent for paint, varnish, in preserving biological specimens, used as a fuel mixed with petrol etc. Though their chemical and physical properties are already studied, still because of their uses in day to day life the authors thought it is better to study some more of their physical properties like ultrasonic velocity and hence adiabatic compressibility, free length, etc. A detailed study of such properties and some excess parameters like excess adiabatic compressibility, excess free volume and few more in the liquid mixtures of these two compounds with PEG as a solute and Ethanol as a solvent at various mole fractions may throw some light on deeper understanding of molecular interaction between the solute and the solvent supported by NMR, IR etc. Hence the present research work is on ultrasonics/allied studies on these two liquid mixtures. Ultrasonic velocity (U), density (ρ) and viscosity (η) at room temperature and at different mole fraction from 0 to 0.055 of ethanol in PEG have been experimentally carried out by the authors. Acoustical parameters such as adiabatic compressibility (β), free volume (V_f), acoustic impedance (Z), internal pressure (π_i), intermolecular free length (L_f) and relaxation time (τ) were calculated from the experimental data. We have calculated excess parameters like excess adiabatic compressibility (β^E), excess internal pressure (π_i^E) free length (L_f^E) and excess acoustic impedance (Z^E) etc for these two chosen liquid mixtures. The excess compressibility is positive and maximum around a mole fraction 0.007 and excess internal pressure is negative and maximum at the same mole fraction and longer free length. The results are analyzed and it may be concluded that the molecular interactions between the solute and the solvent is not strong and it may be weak. Appropriate graphs are drawn.

***Keywords*—**Adiabatic Compressibility, Binary mixture, Induce dipole, Polarizability, Ultrasonic.

I. Introduction

THE ultrasonic technique, due to their simplicity and accuracy is being most widely used in the study of liquid state, the most complicated among the three states of matters. We are engaged in a systematic study of liquid state using a few optoacoustic properties [1]-[3]. Ultrasonic investigation finds extensive application in the characterizing aspects of the physio-chemical behavior of liquid mixtures. In prevailing literature, they have made notable contributions in the study of liquid mixtures [4]-[7]. The kinetic behaviors of chemical and structural equilibrium having constant reaction rate between 10^{-9} to 10^{-4} sec. can be studied by ultrasonic techniques [8]. As these techniques are nondestructive, it plays an important tool for basic and applied research in Physics, Physical Chemistry, Material Science, Biology and Medicine. In the present paper, we discuss about molecular interaction with the help of NMR and IR spectrum in aqueous solution of Poly ethylene glycol (PEG). The molecular weight of PEG and Ethanol are 400 and 46.08 respectively. The molecular formula of PEG and Ethanol are $C_{2n+2}H_{4n+6}O_{n+2}$ and C_2H_5OH respectively. The structural formula of Ethanol is shown in Fig. 1.

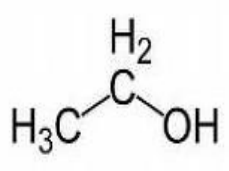

Fig. 1 Structural formula of Ethanol

Mixture of Poly ethylene glycol (PEG) with ethanol has been much studied for their potential application in biochemical and biomedical processes [9]-[11], separation and purification, cell fusion as well as glucose sensoring. Chemical and pharmaceutical applications include the use of PEG as surfactant, base materials of ointments, as antifreezing agent and plasticizer. PEG is used in many industries such as a releasing agent for foam rubber, latex rubber in rubber industries, as a softener in antistatic agent, scouring agent, sizing agent, dying auxiliary, etc in textile industries as well as in metal, wood paper, resin, paint and as a basic substance for the production of cream and hydrogels in cosmetic industries.

PEG is a polymer composed of repeating subunit of ethylene oxide. PEG and its functionalized derivatives can be formed in linear or branched shaped with different molecular masses resulting in a significant material complexity and diversity. Its structural arranged formula $OH\text{-}(CH_2CH_2\text{-}O)_nH$ (n= degree of polymerization) is shown in Fig. 2, the hydrophilic oxygen atom along polymer chain is responsible for its variety of applications. In PEG, both type of hydrogen bonding intra as well as intermolecular hydrogen bonds [12] are found along polymer chain which is responsible for its excellent solubility in ethanol and main organic solvents.

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Adiabatic compressibility or elasticity [13] of liquids is the thermodynamic parameter of fundamental significance. As it depends on the structure of liquids and viscosity, a change in volume follows the applied structure.

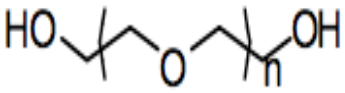

Fig. 2 Structural arranged formula

However, there are two possible ways by which change in structure associated with molecular motion occurs. First and significant structural change occurs due to change in volume resulting from compression when the molecules past each other into a passion of closer packing hence position of molecules changes and time lag arises for rearrangement. A second type of structural change arises due to displacement of molecules about some equilibrium.

In the present paper, densities, ultrasonic velocities and viscosities of binary mixture of Polyethylene Glycol + Ethanol have been studied at room temperature over wide range of mole fractions. From their experimental values, adiabatic compressibility (β), acoustic impedance (Z), internal pressure (π_i), intermolecular free length (L_f) and relaxation time (τ) and their derivations excess adiabatic compressibility (β^E), excess intermolecular free length (L_f^E) and excess acoustic impedance (Z^E) have been calculated. The variation of these parameters with the mole fraction was found to be useful in understanding the nature of interactions between the components.

II. Experimental Procedure

A. Experimental Method

Polyethylene Glycol and Ethanol were of Analar grade and their boiling points agreed well with the literature values indicating that the liquids used in the present study are of high purity. The mixtures were prepared by mixing appropriate weight of the two components in the binary systems and mole fractions were calculated from the number of molecules. The ultrasonic velocities (U) of the above liquids and their mixtures were measured using multi frequency ultrasonic interferometer at a frequency of 2MHz (Mittal Enterprises-model F-81). The accuracy in the measurement of ultrasonic velocity of was within +/- 0.1m accuracy. Oswald's Viscometer was used to measure the viscosities (η) of the solutions. The temperature was maintained constant at room temperature. Acoustical parameters are calculated using standard equations [14]-[17].

B. Theory

Various physical and thermo dynamical parameters were from the measured data such as

Adiabatic Compressibility

$$\beta = \frac{1}{U^2 \rho} \tag{1}$$

Intermolecular Free Length

$$L_f = k\sqrt{\beta}\ , \tag{2}$$

where k is a temperature independent constant. Its value is $4.28X10^9$, at room temperature.

Free Volume

$$V_f = \left(\frac{M_{eff} U}{k\eta}\right)^{3/2} \tag{3}$$

where M_{eff} is the effective molecular weight ($M_{eff}=\sum m_i\ x_i$) in which m_i and x_i are the molecular weight and the mole fraction of the individual constituents respectively). K is a temperature independent constant which is equal to $4.28X10^9$ for all liquids.

Internal Pressure

$$\pi_i = bRT\left(\frac{k\eta}{U}\right)^{1/2}\left(\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right) \tag{4}$$

where b is the cubic packing which is assumed to be 2 for all liquids and solutions,
η is the viscosity and the concentration in gram moles/liter. R is a gas constant and T absolute temperature.

From Ultrasonic relaxation time (τ) following Erings rate process theory, the Gibb's energy can be estimated from:

$$\Delta G = RT\ln\left(\frac{kT\tau}{h}\right) \tag{5}$$

where, R is the gas constant, k is the Boltzman's constant ($1.23x10^{-23}$), T the room temperature, h the Planck's constant and τ is the relaxation time ($\tau = \frac{4}{3}\eta\beta$).

Excess values of the above parameters can be determined using:

$$A^E = A_{exp} - A_{theoreticald} \tag{6}$$

$$A_{Theoretical} = xM_A + (1-x)M_B\ ,$$

where M_A and M_B are the molecular weight of PEG and Ethanol respectively.

TABLE I
VALUES OF DENSITY (P), VELOCITY (U), VISCOSITY (H), AND ULTRASONIC VELOCITY (U), ADIABATIC COMPRESSIBILITY (B), FREE LENGTH (L_F), FREE VOLUME (V_F), MOLAR VOLUME (V_M) INTERNAL PRESSURE (Π_i) FOR PEG+C_2H_5OH

X_1	X_1	U m/s	ρ kg/m^3	ηx10^{-3} Ns/m^2	V_m X10^{-3}	V_f X10^{-3} m^3/mol	M_{eff}	Z X10^6	β x10^{-10} m^2/N	L_f X10^3m	π_i x10^6 N/m^2	ι x10^{12}
0	0	1207	789	1.20	58.403	1.1269	46.08	0.9523	8.7	126.24	9.1774	1.392
	0.007	1138.8	406.3	0.6035	119.52	3.1334	48.56	0.4627	18.98	18.6463	6.0138	1.5271
	0.01	1140	425.4	0.6915	116.64	2.6423	49.62	0.485	18.09	18.2038	6.1411	1.6677
	0.02	1167	458.1	0.8655	116.05	2.1673	53.16	0.5346	16.03	17.1360	6.3246	1.8497
	0.03	1180.4	482.1	1.0463	117.61	1.8	56.7	0.5691	14.89	16.5155	6.449	2.0768
	0.037	1198	505.7	1.1276	117.03	1.7805	59.18	0.6058	13.78	15.888	6.5558	2.0715
	0.04	1206.8	524.2	1.325	114.92	1.4518	60.24	0.6326	13.1	15.491	6.6287	2.3141
	0.05	1224	557.4	1.4943	114.42	1.3486	63.78	0.6823	11.97	14.8078	6.7968	2.3859
	0.055	1240	581.3	1.7513	112.76	1.1292	65.55	0.7208	11.19	14.3172	6.8875	2.6124

m= meter, mol=mole,N=Newton, s=second,kg=kilogram

III. RESULT AND DISCUSSION

The measured values of ultrasonic velocity along with densities and viscosities for the binary system are given in Table I. The plots of ultrasonic velocity against mole fraction of PEG at room temperature are shown in Fig. 3.

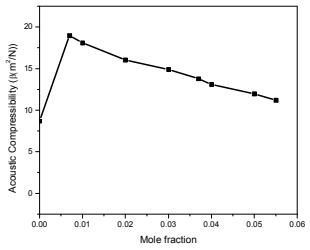

Fig. 3 Variation of Acoustic Compressibility with mole fraction for PEG + Ethanol

This plot is almost linear with positive slope indicating the existence of very weak intermolecular attraction in this system and there is little deviation from the ideal behavior. Adiabatic compressibility (β), intermolecular free length (L_f) and internal pressure (π_i) values were calculated for binary systems investigated and their values are given in Table I. Since adiabatic compressibility is inversely proportional to U^2, the trend in adiabatic compressibility with concentration is the reverse of the trend in ultrasonic velocity with concentrations in the binary systems. Further, the plots of adiabatic compressibility versus mole fraction of PEG shown in Fig. 4 are almost linear suggesting that this system is closed to ideal ones.

Generally the interactions are very weak in dilute solutions and are strong interaction in concentrate solution. In this case, there is weak interaction between the components. The decrease of molecules of β, L_f, and π_i indicates the closer packing of molecules inside the shield.

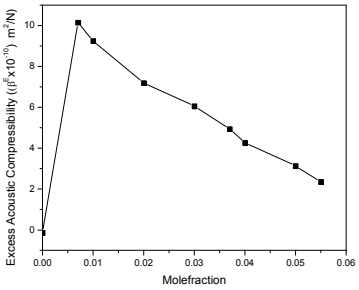

Fig. 4 Variation of Excess Acoustic Compressibility with mole fraction for PEG + Ethanol

The intermolecular free length (L_f) in binary liquid mixtures can be used to assess the attraction between component molecules. The internal pressure (π_i) in binary mixtures is used to access the intermolecular attraction between the components. From Fig. 5 a plot between excess compressibility Vs mole fraction for PEG + ethanol is positive indicating the interactions between the solute and the solvent molecules are not that much strong. As both PEG and ethanol belong to O-H/O-H groups the interaction between them will be repulsive in nature. For confirmation NMR spectrum is taken.

The magnitude and sign of excess parameters can be studied with the strength and the structure making/breaking properties of the liquid mixtures. In this case, excess adiabatic compressibility is decreased with increase of mole fraction. The measured excess values of β^E, L_f^E and π_i^E calculated for the binary system are given in Table II.

TABLE II
VALUES OF EXCESS DENSITY(ρ^E), EXCESS VISCOSITY(η^E), EXCESS ADIABATIC COMPRESSIBILITY(β^E), EXCESS FREE LENGTH(L_f^E), EXCESS FREE VOLUME(V_F^E), EXCESS MOLAR VOLUME (V_M^E), EXCESS INTERNAL PRESSURE (Π_I^E) FOR PEG+C_2H_5OH.

X_1	ρ^E kg/m^3	η^Ex10^{-3} Ns/m^2	V_m^EX10^{-3}	V_f^EX10^{-3} m^3/mol	Z^EX10^6	β^Ex10^{-10} m^2/N	L_f^EX10^3 m	π_i^Ex10^6
0	11	0	-2.987	0	0.0127	-0.137	6.1557	0
0.007	-371.7	-0.6265	58.13	2.0064	-0.4769	10.1431	-101.438	-3.1636
0.01	-352.6	-0.5385	55.25	1.5153	-0.4546	9.2531	-101.8805	-3.0363
0.02	-319.9	-0.3645	54.66	1.0403	-0.405	7.1931	-102.9483	-2.8528
0.03	-295.9	-0.1837	56.22	0.673	-0.3705	6.0531	-103.5688	-2.7284
0.037	-272.3	-0.1024	55.64	0.6535	-0.3338	4.9431	-104.1963	-2.6216
0.04	-253.8	0.095	53.53	0.3248	-0.307	4.2631	-104.5933	-2.5487
0.05	-220.6	0.2643	53.03	0.2216	-0.2573	3.1331	-105.2765	-2.3806
0.055	-196.7	0.5213	51.37	0.0022	-0.2188	2.3531	-105.7671	-2.2899

m= meter, mol=mole,N=Newton, s=second

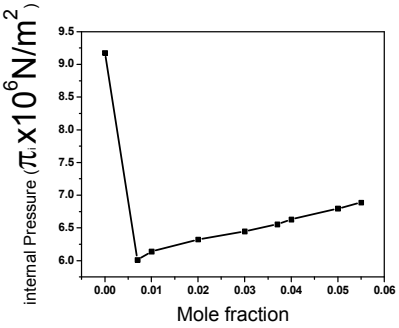

Fig. 5 Variation of internal pressure with mole fraction for PEG + Ethanol

The plots of π_i^E and V_m against mole fraction of PEG at room temperature are shown in Figs. 6, 7. Initially the interaction is weak and towards the increase of mole fraction the interaction becomes stronger due to positive contribution which denotes structure breaking effect.

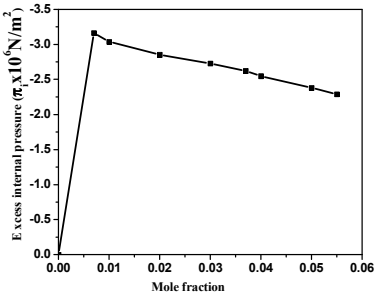

Fig. 6 Variation of Excess internal pressure with mole fraction for PEG + Ethanol

According to Eyring's liquid state theory, the acoustic wave, which was excited in the liquid, is transmitted momentarily to the intermolecular length. In general, when the value of the free volume (V_f) in liquid is large, i.e. the L_f is long, ultrasonic velocity has a low value. Rate process in liquids is determined by the free volume. So, free volume plays an important role in ultra sound wave propagation. The values are reported in Table I.

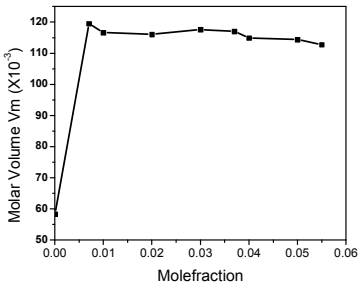

Fig. 7 Variation of Molar Volume with mole fraction for PEG + Ethanol

V_f decreases for the liquids investigated with the increase of pressure, at a constant temperature. In our work, when adiabatic compressibility is decreased with the increasing of mole fraction, the internal pressure is also increased because the value of the free volume (V_f) in liquid is large, the L_f is long and also weak molecular interaction takes place.

The value of capacitance value for air and Ethanol have determined through capacitor of cylindrical tube which is made up of brass metal with the help of LCR meter. The dielectric constant values for ethanol are calculated by the basic formula which is

$$\text{Dielectric Constant for Ethanol } = \frac{C_{air}}{C_{ethanol}} = 25.75,$$

agreeing with the literature values.

But, PEG is a conducting liquid. The electrical conductivity of PEG as measured by us is 5.0μmho/cm.

IV. CONCLUSION

The derived acoustical parameters and their positive values hint to the presence of weak interaction and dispersive interaction between the component molecules in the mixture studied and the inherent nature of alcohols pre-dominate the existing dispersive interactions. NMR and IR spectrum are taken for the same liquid mixture in order to study the molecular interaction and determine the structure of organic compounds.

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