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Absorption and velocity of acoustical waves in binary solutions of poly (ethylene glycol) and water

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The velocity and absorption of ultrasonic waves have been measured in aqueous solutions of poly (ethylene glycol). The velocity of ultrasonic waves was obtained in the frequency range 1MHz-12MHz over a wide range of temperature. The concentration (by weight) ranged from 1% to 10% of poly (ethylene glycol) in water. The shear viscosity was also measured. Measurements were carried out in the temperatures range 35 ^{o}C to 65 ^{o}C. It was observed that velocity of ultrasonic wave increases with temperature at a given concentration, while as concentration is increased at a given temperature, velocity was found to increase. The shear viscosity and density decreased with temperature

1 Introduction

The kinetic behavior of chemical and structural equilibria having reaction rate constant between 10^{-9} to10^{-4} sec. can be studied by ultrasonic techniques [1]. As these techniques are nondestructive, so important tool for basic and applied research in physics, physical chemistry, material science, biology, and medicine. In the present paper we discuss about molecular interactions and elementary processes in aqueous solutions of Poly (ethylene glycol) (PEG).

Mixture of poly (ethylene glycol) with water has been much studied for their potential application in biochemical and biomedical processes [2-4], 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 an antifreezing agent and plasticizer. PEG is used in many industries as a releasing agent for foam rubber, latex rubber in rubber industries, as a softener, 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. As indicated by its structural arranged formula OH-$(CH_2CH_2\text{-}O)_n$H (n=degree of polymerization), the hydrophobic ethylene units are together with hydrophilic oxygen atom along polymer chain which is responsible for its Variety of applications. In PEG, both type of hydrogen bonding (inter as well as intramolecular hydrogen bonds [5]) are found along polymer chain which is responsible for its excellent solubility in water [6] and main organic solvents. Adiabatic compressibility or elasticity [7] of liquids is thermodynamic parameter of fundamental significance. As it depends on structure of liquids and viscosity, because a change in volume following an applied pressure indicate some change in liquid structure. 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 in to 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.

The adiabatic compressibility, κ of a fluid is related to its density, ρ and sound velocity V, (the phase velocity of compressional waves within the sample) according to the equation

$$V = (\rho\,\kappa)^{-1/2} \qquad (1)$$

Hence the ultrasound velocity measurements offer a favorable method to determine the compressibility, κ.

In the present work we have measured ultrasound velocity and absorption, viscosity and density in aqueous solution of PEG in the temperature range 35 ^{0}C to 65 ^{0}C under atmospheric pressure which will be helpful to enhance the knowledge of this aqueous PEG solution as they have for other system [8, 9]

2 Experimental

2.1 Material

PEG was purchased from Sigma Aldrich. Aqueous solution of PEG (with weight average molecular mass 8000 gm/mole) with different concentration by weight was prepared by weighing PEG in required amount. The aqueous solution stirred for 20 hours using a magnetic stirrer to obtain homogeneous solution. No settling was observed even after several weeks.

2.2 Apparatus and measuring procedure

Density was determined by using a calibrated volumetric pycnometer. The uncertainty in the density measurement was found to be about $1x10^{-5}$gm/cm^3. The shear viscosity was determined by using a Ostwald viscometer. Calibration was done by distilled water, Benzene (dried), Methyl alcohol (dried), Acetone (dried). The uncertainty in the viscosity measurement was found to be about 0.1%. The ultrasonic velocities were measured at different temperatures using variable path interferometric technique. The temperature was controlled with thermostatic bath using PID controller with accuracy 0.1^{0}C. In this technique, the sample is kept in a cell, which consists of a double walled metallic jacket having inlet and outlet for circulating thermostatic fluid. An X-cut quartz crystal is fitted in bottom of the cell, which when exited by

RF source produces longitudinal ultrasonic waves which propagates in the medium. These waves are reflected at the metallic reflector, attached to a sensitive micrometer which can be moved up and down with an accuracy of 1μm.The incident and reflected waves form standing wave pattern. By moving the micrometer in the sample, maxima and minima are formed which can be observed in the micrometer of interferometer. These maxima are separated by half integral multiple of the wave length of the ultrasonic wave. The uncertainty in the measurement of the velocity of ultrasonic waves was about 0.03%.

3 Result and discussions

Fig. 1 and 2 show the results for the shear viscosity and density of 10 wt% aqueous solution of PEG as a function of temperature. The viscosity and density decrease with temperature. The changes in the viscosity and density were linear however at the temperature between 55 ^{o}C to 60 ^{o}C, the changes were larger.

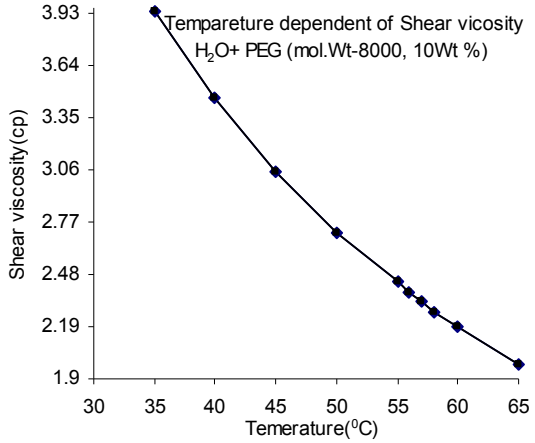

Fig.1 Temperature vs. shear viscosity

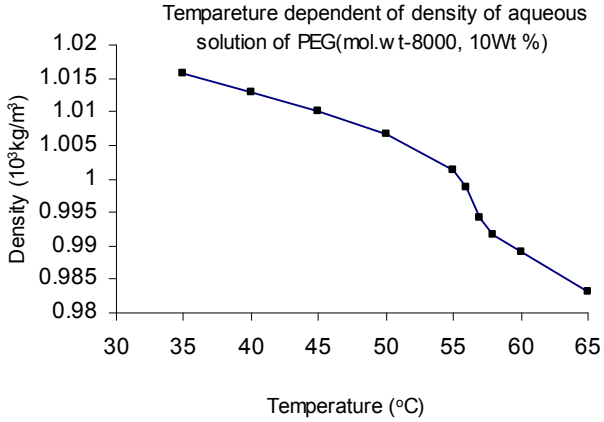

Fig.2 Temperature vs. density

Fig. 3 depicts the results for velocity measurement at different concentrations in aqueous solutions of PEG at 30 ^{o}C. From the figure (3) it can be seen that the ultrasonic velocity increases as the concentration of PEG in water increases, while fig. (4) depicts the dependence of velocity on frequency at different temperatures. From these graphs it can be seen that velocity dispersion occurs in low frequency regime.

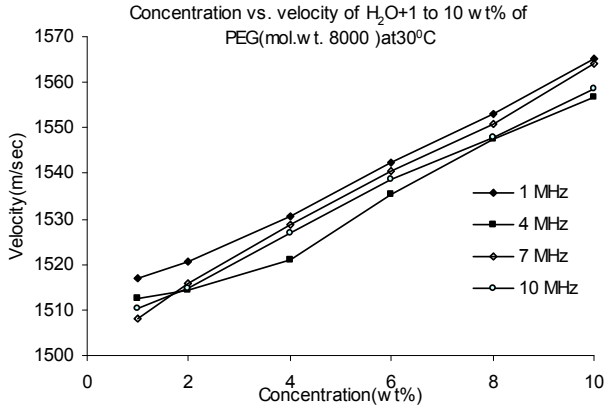

Fig.3 Concentration vs. velocity

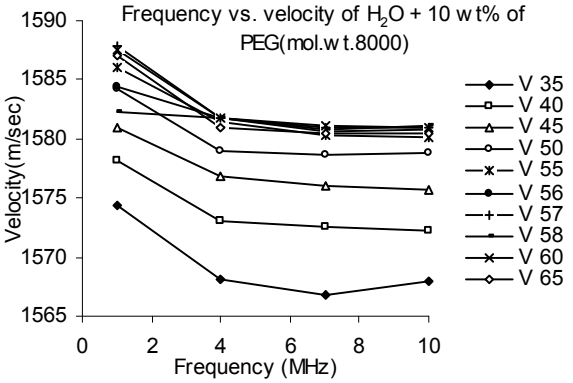

Fig.4 frequency vs. velocity

Ultrasonic velocity decreases at 58 ^{o}C, as density was also decreased in this interesting region. Therefore, it implies that less polymer was added to the water so, concentration, hence velocity decreased. The maximum values of the velocity at this concentration were found at lower temperatures that in water and the velocities at this concentration do not show the same temperature dependence as that of water but shows about 1/6 of the order of magnitudes of the temperature dependence of water. The maximum velocity of water is found to at around 74 ^{o}C [10]. This could be interpreted in terms of changes in the structure of water and in the interaction between polymer and water. The velocities in 10 wt % of aqueous PEG had maximum around 56 ^{o}C to 58 ^{o}C at different frequencies in the temperature range investigated. Willard's work [11] revealed ultrasonic velocity maxima at different temperature in many aqueous solutions.

Measurements of viscosity and density coupled with velocity values have been used to obtain classical ultrasonic absorption. Fig. 5 shows the variation of classical absorption with temperature. From the figure it can be seen that absorption linearly decreases with temperature.

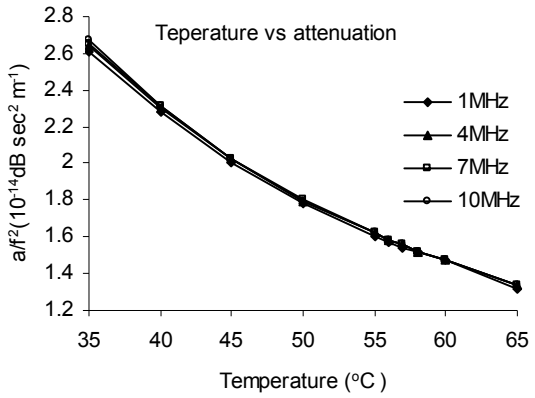

Fig.5 Classical absorption as function of Temperature

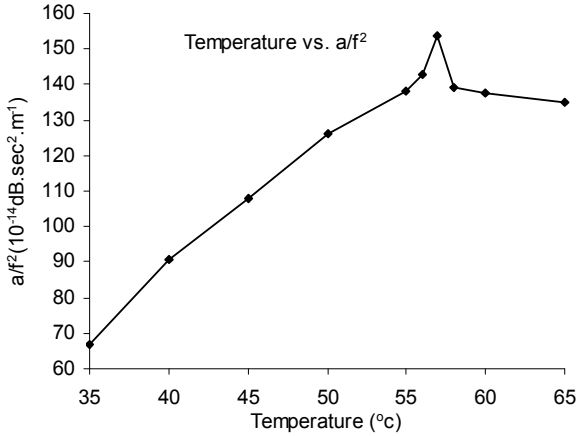

Fig.6 Temperature variation of measured absorption at 5 MHz.

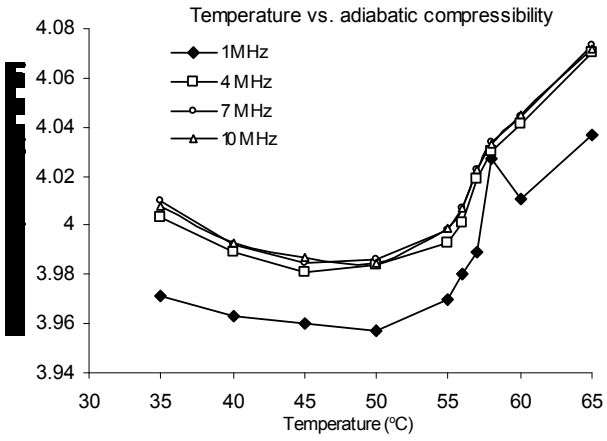

Fig.7 Temperature vs. adiabatic compressibility

From Fig. 6, it can be seen that a/f^2 shows peak at T_m (57^0C), further from fig. (5) and (6) it can be seen that measured value of a/f^2 is large compared to corresponding classical values, which indicates occurrence of some sort of relaxation process. Using Newton-Laplace equation (1), the adiabatic compressibility, κ has been evaluated from sound velocity and density of solution. Fig. 6 shows the result for adiabatic compressibility of PEG-water solution. From fig. (7), it has been seen that first compressibility decreases and becomes minimum and then increases with increasing temperature. The minimum value of compressibility indicates the enhancement of bond strength; however, compressibility at 1 MHz suddenly increases at 58 ^{o}C. It has been suggested that as the velocity is decreased at this temperature which produces sudden increase in the intermolecular free length [12]. It indicates that interaction between the solute and solvent molecules due to which the structural arrangement is considerably changed [13] and forming complexes. The free length increases due to expansion, which indicates that, the looser packing of molecules [12].

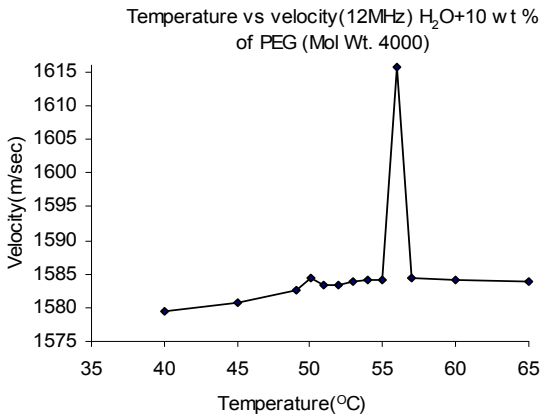

Fig.8 Temperature vs. velocity

Figs. (8), (9) and (10) give the values of velocity of acoustical waves in aqueous solutions of PEG (10 wt %) having molecular weight 2000, 4000 and 8000, respectively at different temperatures .Interestingly, there are sudden change in the velocity at $T_{m.}$. However, the peak associated with T_m is not unique but splitted into two. It is proposed that the PEG forms complex with water in the salvation shell resulting in the second peak. The approximate values of Tm (taking pronounced peak) is 55 ^{o}C, 56 ^{o}C and 57 ^{o}C for PEG of molecular weight 2000, 4000 and 8000 respectively, which is in good agreement with literature values. Hence it is concluded that Tm increases with molecular weight of PEG.

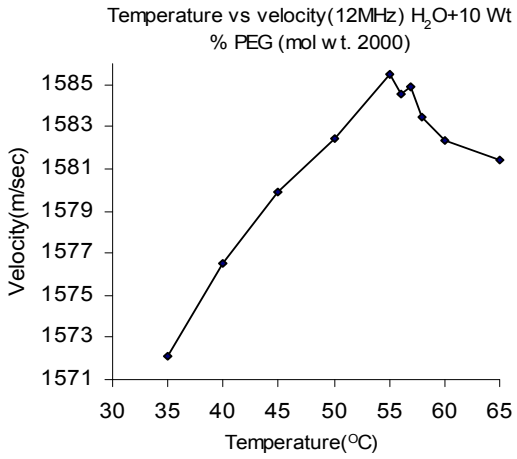

Fig.9 Temperature vs. velocity

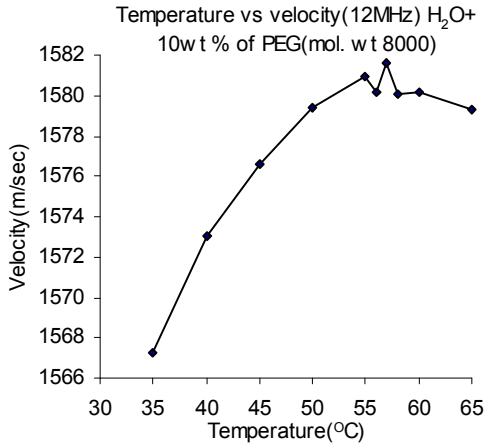

Fig.10 Temperature vs. acoustical velocity

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