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# Acoustical and volumetric investigation of polyethylene glycol 400 and polyethylene glycol 4000 in aqueous solutions of glycerol at different temperatures

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ABSTRACT

The intermolecular interactions of glycerol with two polyethylene glycols i.e. polyethylene glycol 400 and polyethylene glycol 4000 in aqueous medium have been examined from the measurements of density and ultrasonic speed at temperatures $T$ = (293.15, 298.15, 303.15, 308.15) K and experimental pressure $p$ = 0.1 MPa. The apparent molar volume ($V_\phi$), partial molar volume ($V_\phi^o$) and partial molar volume of transfer ($\Delta V_\phi^o$) have been evaluated from density data for polyethylene glycols from water to aqueous glycerol solutions. The limiting apparent molar expansibilities have also been evaluated. The ultrasonic speed measurements are used to determine apparent molar isentropic compression ($K_{\phi,s}$), partial molar isentropic compression ($K_{\phi,s}^o$) and partial molar isentropic compression of transfer ($\Delta K_{\phi,s}^o$) for polyethylene glycols from water to aqueous glycerol solutions. From (partial molar volume and partial molar isentropic compression) of transfer, the pair and triplet coefficients are calculated. By the perusal of these determined parameters, the results have been explicated based upon the competing patterns of physicochemical interactions of co-solutes and the solvents.



## 1. Introduction

For correlating the macroscopic properties and molecular structure of multicomponent liquid mixtures, the thermodynamic acoustic and volumetric study perceives a momentous role [1]. The knowledge of thermodynamic properties is a strenuous tool to identify the mixing effects of numerous chemical compounds and their liquid mixtures. Analysis of such mixtures in terms of molality or mole fraction is imperative for designing several industrial progressions [2]. The modification in the molecular interaction ensues during the formation of liquid mixtures and difference in components' packaging becomes ostensible. When there developed a hydrogen bond network in any of the solvents, then mixture's properties get reformed in a precise manner [3].

An amphiphilic molecule simultaneously possessing the polar and nonpolar group being in aqueous solutions may self-associate to form aggregates known as micelles [4], where the polar group maintains their hydration, and the association between hydrocarbon and water is significantly curtailed. Generally, the hydration (hydrophilic and hydrophobic) properties of the solutes (biomolecules and organic molecules) in aqueous solutions reflect the complex interactions around the solute and the interference of these leads to destructive or beneath specific circumstances, cooperative interactions [5]. Polyethylene glycols, from the group of polymers are the stimulating solvents, owing oxy and hydroxyl groups leads to the formation of inter- and intramolecular hydrogen bonds amongst –O– and –OH group of same or different molecules of Polyethylene glycols (PEGs) [6]. PEGs have considerable range of applications from pharmaceutical to manufacturing industry. PEGs are soluble in aqueous and organic solvents as a result of which they are appropriate for chemical conjugation to biomolecules and end group derivatization [7]. PEG allows a slowed clearance of carried protein from blood when it is attached to a protein medication, hence a longer dosing interval and a longer medicinal effect [8]. To increase the solubility of peptides in organic solvents, Grun *et al.* had examined various strategies by linking up with PEG. It is utilized as a separator in lithium polymer cells, as dispersant in toothpastes, as plasticizers in edible film preparation [9]. In above said applications, the interactions amongst water and PEGs molecules perceives a momentous role and at the same time by adding some cosolute to it, the solvent effects or hydrogen bonding get influenced

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[10–14]. Numerous studies have been done to see the solvation behavior of PEGs in aqueous solutions and with alcohols, ethers, alkoxy benzenes etc. [15,16] but to best of our knowledge, no data has been reported for densities and speeds of sound for PEGs with glycerol. In continuation to our work on glycols [17], in the present study we decided to carry out the volumetric and acoustical study for PEG-400 and PEG-4000 in aqueous glycerol solutions at different temperatures. Glycerol is a polyhydroxy compound comprising 3-dimensional grid of hydrogen bonds has substantial applications in pharmaceutical and food industry as humectant and sweetener [18–24]. In several formulations, it has been practiced as an evaporation regulator and as a cosolvent in cosmetic and pharmaceutical sciences [25,26]. At the time of hydrolysis of lipids in intestine, glycerol acts as a chief biomolecule along with in liver, where it gets involved in metabolism of glucose [27–31]. In manufacturing of vessels for storing various products in pharmaceutical and cosmetic industry, PEGs have a rigorous role. Therefore, it is important to study the interactions among glycerol and PEG molecules. Density and ultrasonic speed data will be utilized to review various physicochemical parameters in terms of solute-solute and solute-solvent interactions prevailing in the present ternary mixtures. The apparent molar properties, partial molar properties and partial molar properties of transfer are determined from the obtained experimental data which give detailed insight about the interactions as well as structure breaking/making tendency of solute (PEGs) in the specified solution.

## 2. Experimental

### 2.1. Materials

The high-grade chemicals used in the present study namely PEG-400, PEG-4000 and glycerol having mass fraction purity better than 0.99, obtained from Loba Chemie Pvt. Ltd were utilized as attained. Nevertheless, to avoid adulteration as a consequence of moisture absorption, the chemicals were dried in vacuum and were kept in desiccators over $P_2O_5$ for no less than 48 h. The detailed description of the chemicals used in the present study is attributed in Table 1.

### 2.2. Apparatus and methods

For preparing solutions, the freshly prepared triple distilled and degassed water having specific conductance $<10^{-6}$ S·cm$^{-1}$ is employed. For determining the density and ultrasonic speed for the prepared samples (using Sartorious CPA 225D balance having a precision of ±0.00001 g), we have used Anton Paar DSA 5000 M densimeter. The uncertainty in the molality of liquid mixtures as per stated purities of the compounds is $u_r(m) = 1\%$. In our former papers [32,33], the details related to calibration and procedures have been specified. At frequency of approximately 3 MHz, the ultrasonic speed measurement was done. The temperature of the device was controlled up to $\pm 1 \times 10^{-3}$ K by a built-in Peltier device, as the density and ultrasonic speed values are extremely sensitive to temperature. The sensitivity of the instrument corresponds to precision in density and ultrasonic speed measurements of $1 \times 10^{-3}$ kg·m$^{-3}$ and $1 \times 10^{-2}$ m·s$^{-1}$. The uncertainties in the measurement of density and speeds of sound are ±0.15 kg·m$^{-3}$ and ±0.5 m·s$^{-1}$, respectively.

## 3. Results and discussion

### 3.1. Volumetric properties

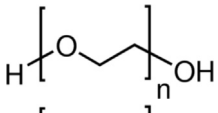
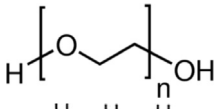
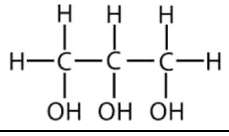
#### 3.1.1. Density

The experimental densities, $\rho$ for PEG-400 and PEG-4000 in (0.00, 0.01, 0.03, 0.05, 0.07) mol·kg$^{-1}$ aqueous solutions of glycerol were measured at temperatures $T$ = (293.15, 298.15, 303.15, 308.15) K and are indexed in Table S1 Supporting information. It has been professed from data that the density values are rising with respect to concentration of PEGs and as well as glycerol. But at a specific concentration of glycerol, the density values are falling relating to temperature. The experimental density values for aqueous PEGs solutions at different temperatures have been compared with literature values [34–38] and the comparison is shown by graph in Figs. 1 and 2. From the Figs. 1 and 2, it is clear that the experimental values are in coherence with literature values. The comparison for the densities of liquid mixtures (glycerol + water) has also been done with the literature values [39–41] and is represented in Fig. 3. The experimental densities are found to be in trend with the literature values given in reference [39,40] but a little deviation has been observed from the values reported in reference [41] at temperature 303.15 K and 308.15 K.

#### 3.1.2. Apparent molar volume

The experimental densities are used to compute the apparent molar volumes ($V_\phi$)utilizing equation (E1) of Supporting Information. The computed apparent molar volumes are attributed in Table S1 Supporting information and all the values are found to be positive. With rising concentration of glycerol, the $V_\phi$ values tend to increase. Also, at a specific concentration of glycerol, the upsurge in values of $V_\phi$ is noticed with regard to upsurge in molality of PEGs and temperature which infers pronounced solute-solvent interactions. The surge in $V_\phi$ values is also perceived in

**Table 1**
Specifications of chemical samples.

| Chemical | CAS number | Molar Mass/ (g·mol$^{-1}$) | Source | Purification method | Mass fraction purity (supplier) | Structures |
|---|---|---|---|---|---|---|
| Polyethylene Glycol 400 | 25322-68-3 | 400 | Loba Chemie Pvt. Ltd, India | Vacuum drying | ≥0.99 |  |
| Polyethylene Glycol 4000 | 25322-68-3 | 3750 (avg.) | Loba Chemie Pvt. Ltd, India | Vacuum drying | ≥0.99 |  |
| Glycerol | 56-81-5 | 92.09 | Loba Chemie Pvt. Ltd, India | Vacuum drying | ≥0.99 |  |