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Volumetric and compressibility properties of liquid water as a solute in glycolic, propylene carbonate, and tetramethylurea solutions at $T = 298.15$ K

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Abstract

The experimental measurements of the speed of sound and density in binary solutions of ethylene glycol, propylene glycol, propylene carbonate, and tetramethylurea (as solvents) and water as the solute in the concentration range of $0.1\ \text{mol} \cdot \text{kg}^{-1}$ to $1\ \text{mol} \cdot \text{kg}^{-1}$ at $T = 298.15$ K are reported. The data are used to obtain the isentropic compressibility (β_S) of solutions. The apparent molar volume (ϕ_V) and compressibility (ϕ_{K_S}) of water at different concentrations of water are evaluated. The data of limiting partial molar volume (ϕ_V°) and compressibility ($\phi_{K_S}^\circ$) of water and their concentration variation are examined to study the effect due to water–solvent and water–water interactions. It has been observed that there is a loss of volume as well as of compressibility of liquid water molecules in transferring them from the pure liquid state to a non-aqueous solvent except for propylene carbonate (in case of volumes). The data are compared with similar data obtained for water in alcohols and other apolar solvents like dioxane, acetonitrile, and dimethylformamide. A possible interpretation has been advanced on the basis of H-bonding characteristics and other structural details of the solvents and water to account for the effects due to water–water and water–solvent interactions.

Keywords: Glycols; Propylene carbonate; Tetramethylurea; Isentropic compressibility; Apparent molar volume

1. Introduction

Water is singular as a liquid because of its ability to form three-dimensional network of molecules, mutually hydrogen bonded [1,2]. From the point of view of H-bonding interactions, hydrophobic interactions (association of non-polar groups in presence of water) and ion–water (dipole) interactions, binary aqueous solutions of variety of electrolytes, non-electrolytes, etc. have been studied in detail [3,4]. However, such studies for water as a solute in organic polar and organic non-polar solvents are very much limited [5–7].

Recently, we undertook a comprehensive programme of making volumetric, compressibility and dielectric constant property measurements for binary solutions involving solvents such as alcohols, apolar THF, dioxane, acetonitrile, benzene, etc. and water as a solute in the concentration range of $0.1–1\ \text{mol} \cdot \text{kg}^{-1}$ of water at $T = 298.15$ K [8,9] for solutions having enough solubility or up to the saturation if solubility is limited. Our dielectric studies revealed that water dissolves in benzene may be in cyclic trimer form exhibiting trimer–monomer type of dissociative equilibria [9]. We also examined possibilities of the presence of water-centered complexes or participation of water in the chain like solvent structure (alcohols) and in apolar solvents like THF, dioxane, acetonitrile and DMF on the basis of volumetric and compressibility studies [8]. We observed that in aqueous methanolic and aqueous ethanolic solutions water exhibits differences in excess volumes and compressibilities as compared to other apolar solvents because of the presence of H-bonded linear structures of

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the solvents themselves. Thus, while the behaviour of alcohols is rather different from that of simple, non-associating liquids [10] no unusual properties ascribable to three-dimensional structures are to be expected. The situation is different with slightly more complex molecule such as ethylene glycol. In this substance, due to the presence of two –OH groups per molecule, one might conceive the formation of three-dimensional networks [11]. Thus, *a priori*, physical and solvent properties intermediate between those of water and the monohydric alcohols are to be expected. Similarities between water and ethylene glycol are also suggested by studies of protein denaturation, ethylene glycol is a much weaker denaturant than other monohydric alcohols [12]. The conformational analysis of ethylene glycol molecule has shown that sufficient number of molecules exist in non-hydrogen bonded conformations forming intramolecular hydrogen bonds, allowing the possibility of three-dimensional structure formation [11].

Therefore in continuation of our work related to studies of interactions of water in organic solvents, we have now extended it to the solutions of water in diols (glycols), propylene carbonate (PC) and tetramethylurea (TMU), propylene carbonate has been used extensively as a reference solvent (relative permittivity = 64.7) to understand the solvation enthalpy effects and other thermodynamic transfer functions (from water to other non-aqueous solvents) in terms of the important interactions like ion–solvent, ion–ion, polarization–dipole and dipole–dipole for electrolyte and non-electrolytes like alcohols [13–15]. Tetramethylurea is a liquid at room temperature, having four methyl groups and a relative permittivity of 23.4 at $T = 298.15$ K. It is widely used as a reaction medium for organic synthesis [16]. We report in this communication, the sound speed and density measurements carried out for solutions (up to $1 \text{ mol} \cdot \text{kg}^{-1}$) involving water as a solute at $T = 298.15$ K. The data are used to obtain isentropic compressibility (β_S) of solution and apparent molar volume (ϕ_V) and apparent molar isentropic compressibility (ϕ_{K_S}) of water as a function of concentration of water. The appropriate determination of partial/apparent molar volume and compressibility of water at infinite dilution (ϕ_V° and $\phi_{K_S}^\circ$, respectively) and its variation with concentration yield information about water–solvent and water–water interactions. These aspects are presented and discussed below.

2. Experimental

EG and TMU were procured from MERCK (purity of about 0.99 mass fraction each), PG was procured from Thomas Baker (purity greater than 0.995 mass fraction) while PC was procured from s.d.fine (purity of about 0.99 mass fraction). These solvents were used without any further purification.

In pure solvents the water concentrations were determined using a microprocessor based automatic Karl–Fischer Titrator, TKF-55, Chemito from the M/s Toshniwal company. Pyridine free Aquanil-5 Karl–Fischer reagent of Thomas Baker was used for analysis. The reagent was standardized with a solution of water in MeOH. The instrument was able to detect water content of the order of ±2 ppm in organic solvents. The water content found for the solvents EG, PG, PC and TMU were of the magnitude of 967, 886, 258 and 298 ppm, respectively.

Densities of all the liquids and solutions of water in organic solvents were determined using a high precision Anton PAAR DMA 60/602 digital densitometer at $T = 298.15$ K. The uncertainty in density measurement was found to be of the order of $\pm 1 \cdot 10^{-2} \text{ kg} \cdot \text{m}^{-3}$. The reliability of density data was checked by determining density values for the various solvents used. The values obtained for EG, PG, PC and TMU were 1109.41, 1032.87, 1198.64, and $963.01 \text{ kg} \cdot \text{m}^{-3}$, respectively, and found to be in good agreement with literature data [14,17]. The minimum assays of water content were also considered, while preparing the solutions of water in organic solvents. The water used for the preparation of solutions was freshly prepared doubly quartz distilled deionized water. All the solutions were prepared on a molality basis. The uncertainty in composition was found to be of the order of $\pm 1 \cdot 10^{-4} \text{ mol} \cdot \text{kg}^{-1}$.

Speed of sound measurements were carried out for solutions of water in organic solvents at $T = 298.15$ K using an Ultrasound interferometer operated at 2 MHz frequency, (M/s Mittle Enterprises). Good quality thermostating (temperature inside the cell ±0.05 K) to maintain constant temperature was achieved by circulating water by means of a Julabo thermostat having an accuracy of ±0.02 K around the cell. The reproducibility in speed of sound measurement was found to be better than $\pm 0.5 \text{ m} \cdot \text{s}^{-1}$ in individual values. The values obtained for pure liquids, i.e., EG, PG, PC and TMU are 1656.1, 1510.6, 1443.4, and 1397.6 $\text{m} \cdot \text{s}^{-1}$, respectively, and in good agreement with the literature data available for EG ($1654 \text{ m} \cdot \text{s}^{-1}$) [18].

3. Results

The variations of the speed of sound parameter ($\Delta u = u_{\text{solution}} - u_{\text{solvent}}$) as a function of the molality of water in EG, PG, PC, and TMU are shown in Fig. 1. Isentropic compressibility (β_S) of solvents and solutions were obtained using the Laplace equation $\beta_S = 1/(u^2\rho)$. The variations of β_S values with the molality of water are shown in Fig. 2. The uncertainty in $\beta_S(\delta\beta_S)$ values was obtained using method of propagation of errors and standard deviations obtained for the experimental parameters including concentration and density of pure solvent; the corresponding equation obtained in this way is

$$\delta\beta_S = \beta_S\left[\left(\frac{2\delta u}{u}\right)^2 + \left(\frac{\delta\rho}{\rho}\right)^2\right]^{1/2} \tag{1}$$

and were found to be of the order of $\pm 0.03 \cdot 10^{-11} \text{ Pa}^{-1}$ for TMU whereas the uncertainty is comparatively small in other systems.