

## Abstract

In this work, the results of densimetric and sonochemical studies of aqueous solutions of 1,5-pentanediol (1,5-PD), diethylene glycol (DEG), triethylene glycol (T3EG) and tetraethylene glycol (T4EG) are presented.

The research was carried out within the entire water – organic mixtures range of composition. The densities of the mixtures were determined within the temperature range 278,15 K – 333,15 K and the sound velocity values of the tested water-organic mixtures were investigated within temperature range 288,15 K – 318,15 K. The obtained experimental values of density and ultrasonic speed in the tested range of composition allowed for the calculation of the excess molar thermodynamic quantities, as well as the apparent and partial molar quantities of the mixture components, describing their properties. The observed changes with a water – organic mixture compositions and temperature are a sensitive indicator of the ongoing changes in the interactions between the mixture components. Consequences of these interactions are structural transformations that take place in the mixtures.

The results of densimetric studies allowed for the calculation of the following quantities:

- excess molar volume of the tested mixtures ( $V_m^E$ ),
- partial molar volume of individual components of the mixtures ( $V_{m,j}$ )
- apparent molar volume of the organic component of the mixture ( $V_{\phi,m,2}$ ),
- coefficient of isobaric thermal expansion of the solution ( $\alpha_p$ ) a
- and its excess ( $\alpha_p^E$ ),
- molar isobaric thermal expansion of the solution ( $E_{p,m}$ ) and its excess ( $E_{p,m}^E$ ).

Observed changes in the quantities mentioned above, both in relation to the composition of the mixture and the temperature, were carefully analysed. The differences were discussed in the context of changes in the interactions between the mixture components, and their influence on the stability and degree of packing of formed structure. The values of the ultrasonic sound speed and its deviations from additivity were analysed for all tested mixtures depending on their composition and temperature (288,15 K – 318,15 K). The compositions of the mixtures, in which the interactions between the molecules of water and the organic component of the mixture are the strongest and lead to the formation of a stable and stiffened structure, were found. The combination of

densimetric and sonochemical results for all investigated mixtures at selected temperatures enabled the calculation of:

- isentropic compressibility factor ( $\kappa_S$ ) of mixtures and their excess ( $\kappa_S^E$ ),
- molar isentropic compressibility ( $K_{S,m}$ ) of mixtures and their excess ( $K_{S,m}^E$ ),
- hydration numbers of the tested organic compounds in individual solutions.

Noticed changes of the quantities mentioned above with the composition of the mixture and temperature were discussed in terms of changes in intermolecular interactions, affecting stability of the mixture structure. The phenomenon of hydration of the molecules of the tested substances was connected with the number of oxyethylene groups contained in their chain. Under isothermal conditions, it was analysed how pressure can affect changes in basic molar thermodynamic quantities, such as Gibbs energy, enthalpy, entropy, and isobaric molar heat capacity. For this purpose, the excess of the derivatives of the quantities mentioned above as a function of pressure at the temperature of 298,15 K were calculated. Their changes with the composition of individual mixtures, taking into account the differences in the molecular structure of the organic component of the mixture, were discussed. It was described how replacing the methylene group in the  $\gamma$ -position in the 1,5-pentandiol molecule for the ether oxygen atom, as well as extending the chain of molecule with subsequent oxyethylene groups, changes the differences in the excesses of selected physicochemical quantities such as:

- molar volume ( $\Delta V_m^E$ )
- coefficient of isobaric thermal expansion of the solution ( $\Delta \alpha_p^E$ ),
- molar isobaric thermal expansion of the solution ( $\Delta E_{p,m}^E$ ),
- isentropic compressibility factor of the solution ( $\Delta \kappa_S^E$ ),
- molar isentropic compressibility of the solution ( $\Delta K_{S,m}^E$ ).

The results of the research carried out in this work made it possible to determine the conditions (the composition of the mixture and the temperature) at which significant changes in intermolecular interactions occur and relate them with structural changes occurring in the solution.