EXPERIMENTAL STUDY OF THE DENSITY AND DERIVED (EXCESS, APPARENT, AND PARTIAL MOLAR VOLUMES) PROPERTIES OF BINARY WATER+ETHANOL AND TERNARY WATER+ETHANOL+LITHIUM NITRATE MIXTURES AT TEMPERATURES FROM 298 K TO 448 K AND PRESSURES UP TO 40 MPA

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Accurate volumetric (density, excess, apparent, and partial molar volumes) data of aqueous solutions is crucial for understanding many industrial and natural processes. In many applications these processes occur at high temperatures and high pressures. Most previous high-pressure density measurements were performed using VTD technique [1, 2, 3] with typical uncertainty of 10-4 g⋅cm-3 and cover very limited concentration range (basically dilute mixtures) and pressures up to 40 MPa. Constant –volume piezometer was used in the works [4,5] for high temperature (up to 673 K) and high pressure (up to 60 MPa) density measurements, including supercritical region. The uncertainty of these measurements is within 0.03 % to 0.15 % depending on temperature and pressure ranges. In our previous work [5] we have measured *PVTx* relationship of the water+ethanol mixtures in the wide temperature (from 423 to 673 K) and pressure (up to 51 MPa) ranges using constant-volume piezometer immersed in air thermostat with an uncertainty of 0.15 %. The derived values of density were used to calculate derived volumetric properties such as excess, partial and apparent molar volumes. In these works the values of  and were obtained using the measured mixtures densities at infinite dilutions. The values of for most water+alcohol solutions decrease with concentration which is related to the degree of hydrophobicity of the alcohol molecular.

The excess (), apparent () and partial () molar volumes are very useful tools for understanding the interactions between the solute and solvent molecules occurring in the mixtures. Alcohol is the standard example of associated fluids. Alcohol molecules strongly affect water structure which leads to anomaly of the thermodynamic properties of the water+alcohol mixtures. Alcohol molecules re-building water’s structure which is leading considerable changing thermodynamic properties of aqueous alcohol mixture. Studies of the apparent and partial molar volumes of aqueous mixtures are used to examine solute-solvent, solute - solute, and solvent-solvent (structural) interactions, *i.e.*, provide useful information on the nature of interaction between solute and solvent molecules. The excess properties, like, reflect of the origin of the non-ideality in the mixture, especially in the mixtures that show strong interactions between the unlike (solute and solvent) molecules. The volumetric properties (density, excess and partial molar volumes) are providing very useful information on the structural and intermolecular interaction between the solvent and solute molecules with different sizes, shapes, and chemical nature. For deeply understanding of the nature and physical and chemical mechanism of aqueous alcohol mixture properties anomalies the accurate experimental study of the volumetric properties are needed.

This work is a part of our studies on the thermodynamic properties of aqueous electrolyte systems under high temperatures and high pressures. The present work presents experimental densities of binary water+ethanol and ternary water+ethanol+lithium nitrate mixtures as a function of the molality of the electrolyte (LiNO3) and the electrolyte-free mass fraction of the ethanol at temperature from (298 to 448) K and at pressures up to 40 MPa. As part of our study of aqueous mixtures of electrolyte, in the present work we measured volumetric properties of the ternary mixtures water+ethanol+lithium nitrate.

Densities of binary water+ethanol and ternary water+ethanol+LiNO3 mixtures have been measured over the temperature range from 298 K to 448 K and at pressures up to 40 MPa using the constant-volume piezometer immersed in a precision liquid thermostat. The experimental details (apparatus, procedure of the measurements, and detailed uncertainty assessment procedure) of the density measurements have been described fully in our previous publications.

New density data for liquid water+ethanol mixtures have been measured over the temperature range from 298 K to 448) K and at pressures up to 40 MPa using the constant-volume piezometer technique for dilute mixtures (for four compositions of 0.0163, 0.0343, 0.0730, and 0.0946 mole fraction of ethanol). The measurements for ternary water+ethanol+LiNO3 mixtures were performed in the same temperature and pressure ranges for twelve concentrations of LiNO3 (0.520, 0.940, 0.0457, 0.4757, 0.8599, 1.0931, 0.0422, 0.4387, 0.7930, 1.1870, 0.5200, and 0.9400 mol⋅kg-1). Good agreement (within 0.02 % to 0.05 %) is found between the present density measurements for the mixture and the data sets reported by other authors in the literature. The derived volumetric properties such as excess (), apparent (), and partial () molar volumes at infinite dilution were calculated using the measured density data for the water+ethanol mixture and pure water (IAPWS) and pure ethanol as a function of temperature, pressure, and concentration. The values of excess molar volume for water+ethanolmixtures are small (maximal value is about -1.12 cm3⋅mol-1) and negative at all measured temperatures, pressures, and over the entire concentration range. The excess molar volume minimum is found at concentration about 0.4 mole fraction of ethanol (slightly skewed towards low concentrations). Derived values of apparent molar volume of water+ethanolmixtures at low concentration range (dilute mixture) decreases with concentration, passes through a minimum around 5 mol⋅kg-1, and then rapidly increases at higher concentrations. The locus of the concentration minimum shifted to the low concentration range with temperature increasing and finally at 348 K is vanished. The location of the concentration minimum of is almost independent on pressure.

Density measurements were made at constant temperatures as a function of pressure. The experimental density results for water+ethanol and water+ethanol+LiNO3 mixtures are shown in Figs.1



**Fig. 1.** Measured densities of aqueous ethanol mixtures as a function of pressure along the various isotherms for two selected concentrations.

**Left**: ●,297.05 K;○, 323.15 K; ■, 348.15 K; □, 373.15 K; ▲, 398.15 K; △, 423.15 K; ⯁, 448.15 K.

**Right**: ●,298.15 K;○, 323.15 K; ■, 348.15 K; □, 373.15 K; ▲, 398.15 K; △, 423.15 K; ⯁, 448.15 K. Dashed lines are interpolated data.

The temperature dependences of the present measured densities for aqueous ethanol mixtures along the two selected isobars (10 and 40 MPa) and for various concentrations are shown in Fig. 2 together with the pure water values calculated from IAPWS for the same isobars.



**Fig. 2.** Measured densities of aqueous ethanol mixtures as a function of temperature along the two selected isobars for various concentrations. ○, 10 MPa;●,40 MPa;Solid lines are pure water values calculated from IAPWS. Dashed lines are interpolated data.

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