



Densities and volume properties of (water + tert-butanol) over the temperature range of (274.15 to 348.15) K at pressure of 0.1 MPa

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ABSTRACT

The densities of {water (1) + tert-butanol (2)} binary mixture were measured over the temperature range (274.15 to 348.15) K at atmospheric pressure using “Anton Paar” digital vibrating-tube densimeter. Density measurements were carried out over the whole concentration range at (308.15 to 348.15) K. The following volume parameters were calculated: excess molar volumes and thermal isobaric expansivities of the mixture, partial molar volumes and partial molar thermal isobaric expansivities of the components. Concentration dependences of excess molar volumes were fitted with Redlich–Kister equation. The results of partial molar volume calculations using four equations were compared. It was established that for low alcohol concentrations at $T \leq 208$ K the inflection points at $x_2 \approx 0.02$ were observed at concentration dependences of specific volume. The concentration dependences of partial molar volumes of both water and tert-butanol had extremes at low alcohol content. The temperature dependence of partial molar volumes of water had some inversion at $x_2 \approx 0.65$. The temperature dependence of partial molar volumes of tert-butanol at infinite dilution had minimum at ≈ 288 K. It was discovered that concentration dependences of thermal isobaric expansivities of the mixture at small alcohol content and low temperatures passed through minimum.

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1. Introduction

The properties of {water + tert-butanol (tertiary butyl alcohol, TBA)} systems are of intent interest. Firstly, tertiary butyl alcohol is the only isomer of butyl alcohols which is soluble indefinitely in water at atmospheric pressure. Secondly, the dependences of many thermodynamic characteristics of (water + tert-butanol) mixtures on mixture composition have sharp extremes at very low alcohol concentrations. Thirdly, the tert-butanol molecule is, in some way, a model one, i.e. it can be considered as methanol derivative with hydrogen atoms replaced by methyl-groups. In the alcohol molecule three hydrophobic $-\text{CH}_3$ groups are responsible for hydrophobic effects in water and one hydrophilic $-\text{OH}$ group is able to form strong H-bond both with water and with other tert-butanol molecules. Fourthly, in tert-butanol nonspecific interactions are very strong, e.g. among other butyl alcohols it has the highest freezing point (298.65 K) and the lowest boiling temperature (355.35 K) [1–4].

Volume properties of {water (1) + tert-butanol (2)} mixture were investigated earlier by many authors [5–22] but these data are rather scattered. So the most part of these studies dealt with

solutions of low alcohol concentration [12–17] or measurements were carried out at 298.15 K only [5–11]. In spite of the fact that TBA freezing temperature is higher of 298.15 K, in some works densities of liquid tert-butanol are presented at 298 K and even lower [23]. This demonstrates mainly the low quality of the alcohol used. In the works [11,18] the results of density measurements are presented just graphically. The data on density determined at different temperatures and over the whole concentration range are given in papers [19–22]. The density of (water + tert-butanol) system was measured using pycnometers at (288.15, 298.15, 313.15, and 323.15) K by Kenttamaa and co-workers [19]. Hvidt *et al.* [20] have measured the density using vibration densimeter with accuracy up to $\pm 1 \cdot 10^{-5} \text{ g} \cdot \text{cm}^{-3}$ at temperatures of (278.15, 283.15, 293.15, and 298.15) K and up to the alcohol content of 0.56 mole fraction. The densities at atmospheric pressure were determined by Kubota *et al.* [21] at (298.15, 323.15, and 348.15) K and at five mixture compositions ($x_2 = 0.05, 0.1, 0.25, 0.50, 0.75$). Kim and Marsh [22] using pycnometers have measured the density at (303.15, 308.15, 313.15, 318.15, and 323.15) K over the entire concentrations range (36 compositions) with accuracy of $\pm 1 \cdot 10^{-5} \text{ g} \cdot \text{cm}^{-3}$.

For reasons given above it can be concluded that a majority of experiments on volume properties of (water + TBA) mixtures performed earlier were carried out either at one temperature, or over

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the short temperature or concentration range, or over the whole concentration range but with large intervals. These data cannot be used for careful calculation of thermal isobaric expansivities and its partial values for components, as well as partial molar volumes cannot be found from the data.

The present work is a continuation of our earlier researches of volume properties of binary systems with different nature of interactions depending on composition, temperature and pressure [24–33].

2. Experimental

All mixtures were prepared gravimetrically from degasified solvents. All preparations and density measurements were carried out without a contact of solutions with atmospheric air. Only fresh-made solutions were used for all measurements. Tert-butanol (stated purity 0.995) was purified by double distillation according to [2,3] and was kept under vacuum. Water content in the alcohol was determined with K. Fisher method and did not exceed of 0.015 wt.% (or 0.00004 mole fraction).

Densities (ρ) were measured with vibration densimeter Anton Paar DMA-4500. Every measurement was preceded by densimeter calibration with dry air and doubly-distilled degasified water. The density was measured over the temperature range from (274.15 to 348.15) K. At temperatures of (308.15, 323.15, 333.15, and 348.15) K the densities were measured over the entire concentration range (for 36 mixture compositions). In the region of low TBA concentrations the densities were measured additionally at temperatures from (274.15 to 283.15) K with an interval of 1 K.

The error of mixtures preparation was less of $2 \cdot 10^{-5}$ mole fraction. The temperature was kept within ± 0.01 K. The reproducibility of density values was of $1 \cdot 10^{-5} \text{ g} \cdot \text{cm}^{-3}$. The total uncertainty of density determination was not exceeding of $5 \cdot 10^{-5} \text{ g} \cdot \text{cm}^{-3}$.

In figure 1 the relative deviations of tert-butanol density obtained in this work from literature data are plotted. The maximum of deviation within temperature range of (303.15 to 323.15) K, with the largest number of measurements, varies in the range from +0.025% to –0.09%, and is equal to –0.21%, according to [21], at 348.15 K. The best agreement is observed with results obtained in works [22,34]. With temperature growth the relative deviation of experimental densities from the values obtained in [22]

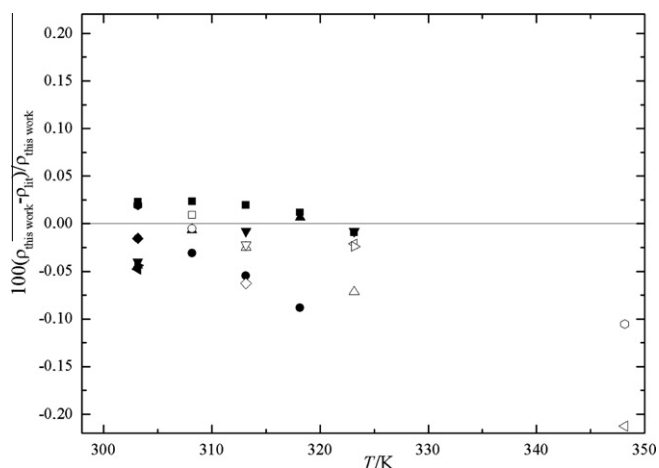


FIGURE 1. Relative deviations of density experimental values obtained in this work from different literature data: (■) Kim and Marsh [22]; (●) Nain [23]; (▲) Martinez et al. [34]; (▼) TRC Thermodynamic Tables [66]; (◆) Nikam et al. [67]; (◀) Ahlam et al. [68]; (▶) Martinez et al. [69]; (◐) Brown and Smith [70]; (□) Sakurai [18]; (○) Anson et al. [71]; (△) Kenttaamaa et al. [19]; (▽) Weng [72]; (◇) Giner et al. [73]; (◁) Kubota et al. [21]; (▷) Langa et al. [74]; (◊) Harris et al. [75].

increases and it decreases as compared with density values from [23]. However, the common tendency is observed, namely the higher the temperature the larger the literature density values in comparison with data of present work.

Experimentally determined densities of (water + TBA) mixture over the temperature range from (274.15 to 348.15) K at atmospheric pressure are given in the table 1.

3. Results

Excess molar volumes, V_m^E , were calculated directly from experimental data by equation (1):

$$V_m^E = x_1 M_1 (1/\rho - 1/\rho_1) + x_2 M_2 (1/\rho - 1/\rho_2), \quad (1)$$

where x_1 , M_1 , ρ_1 , and x_2 , M_2 , ρ_2 are molar fractions, molar masses, and densities of water and TBA, accordingly, ρ is a mixture density. The uncertainty of excess molar volume determination did not exceed of $\pm 0.02 \text{ cm}^3 \cdot \text{mol}^{-1}$.

Concentration dependences of excess molar volumes, V_m^E , were fitted by Redlich–Kister equation (2) [35,36]:

$$V_m^E = x_1 x_2 \sum_{i=0}^{i=n} A_i (x_1 - x_2)^i, \quad n = 6. \quad (2)$$

The optimal degree of the equation, n , was determined by standard deviation, σ , being calculated by equation:

$$\sigma = \left[\sum (V^E - V_{\text{cal}}^E)^2 / (N_{\text{exp}} - n) \right]^{1/2}, \quad (3)$$

where N is the number of experimental points, n is the polynomial degree. The adjustable parameters, A_i , of equation (2) along with the standard deviations, σ , at every temperature are performed in table 2.

Apparent molar volumes of water, $V_{\phi 1}$, and of TBA, $V_{\phi 2}$, for every isotherm were calculated directly from experimental data by equations (4) and (5):

$$V_{\phi 1} = \frac{(\rho_2 - \rho)x_2 M_2}{x_1 \rho \rho_2} + \frac{M_1}{\rho}, \quad (4)$$

$$V_{\phi 2} = \frac{(\rho_1 - \rho)x_1 M_1}{x_2 \rho \rho_1} + \frac{M_2}{\rho}. \quad (5)$$

Extremes at concentration dependences of apparent and partial molar volumes of (water + TBA) mixtures, firstly, are observed at very low alcohol concentrations ($x_2 \approx 0$) and, secondly, appear within very narrow concentration range. Because of such extremal shape of concentration dependences the partial molar volumes of components were found by using several equations including conversion of molar fractions, x_i , to mass ones, w_i . Such approach was used because the approximation of experimental points, located in the region of very low alcohol concentrations and forming some extreme dependence, is interpreted at mathematical treatment as data with large uncertainties and not as extreme.

Partial molar volumes of components, \bar{V}_1 and \bar{V}_2 , were calculated by equations (6)–(13)

$$\bar{V}_1 = V_m - x_2 (\partial V_m / \partial x_2), \quad (6)$$

$$\bar{V}_2 = V_m - x_1 (\partial V_m / \partial x_1), \quad (7)$$

$$\bar{V}_1 = V_{\phi 1} + x_1 x_2 (\partial V_{\phi 1} / \partial x_1), \quad (8)$$

$$\bar{V}_2 = V_{\phi 2} + x_1 x_2 (\partial V_{\phi 2} / \partial x_2), \quad (9)$$

$$\bar{V}_1 = M_1 (1/\rho + (1 - w_1) \partial(1/\rho) / \partial w_1), \quad (10)$$

$$\bar{V}_2 = M_2 (1/\rho + (1 - w_2) \partial(1/\rho) / \partial w_2), \quad (11)$$

$$\bar{V}_1 = V_m^E + V_1^o + x_2 (\partial V_m^E / \partial x_1), \quad (12)$$

$$\bar{V}_2 = V_m^E + V_2^o - x_1 (\partial V_m^E / \partial x_1). \quad (13)$$

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