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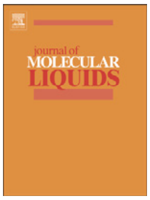

Volumetric properties of the binary mixture of ethylene glycol + *tert*-butanol at $T = (278.15, 288.15, 298.15, 308.15, 323.15, 333.15, 348.15)$ K under atmospheric pressure

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ABSTRACT

Densities of ethylene glycol(1) + *tert*-butanol(2) mixtures were measured between (278.15–348.15) K at atmospheric pressure over the entire composition range with a vibrating tube densimeter. It was found that specific volume of mixture increases with growth of *tert*-butanol concentration at all temperatures under study. Excess molar volumes, apparent and partial molar volumes of ethylene glycol and *tert*-butanol, coefficients of isobaric expansion of mixture and partial molar isobaric expansion of the components were calculated. Excess molar volumes of the mixture are negative at all temperatures, and deviation from ideality is increased with temperature rise. Excess molar volumes were described by Redlich–Kister equation. Partial molar volumes of ethylene glycol decrease sharply at $x_2 \to 1$. Temperature dependence of partial molar volumes of ethylene glycol is characterized by inversion at $x_2 \approx 0.7$. The “negative expansion” of limiting partial volumes of ethylene glycol was observed. Coefficients of isobaric expansion of the mixtures increased with rise both of *tert*-butanol concentration and temperature.

1. Introduction

Volumetric properties of liquid mixtures are a constitutive information source for characterization of interactions between their components. Properties of these systems significantly change under appearance of hydrogen bond network. Solvents with spatial network of hydrogen bonds are characterized by relatively large free volumes, small values of isothermal compressibility and isobaric thermal expansivity as well as by high viscosity. Ethylene glycol mixed with water is referred to the systems with spatial network of hydrogen bonds [1–7]. It is well known that in many cases composition dependences of the properties of *tert*-butanol aqueous solutions display sharp extremes in the range of small amounts of the alcohol [8–20]. This phenomenon is caused by the occurrence of hydrophobic effects [21,22]. Therefore, it is interesting to study volumetric properties of ethylene glycol + *tert*-butanol mixture.

Ethylene glycol (EG) ($\varepsilon = 34.5$, $\mu = 2.28$ D, $\eta = 20.8$ mPa·s at 293 K; $T_{\text{melting}} = 260.55$ K; $T_{\text{boiling}} = 471.0$ K) [23,24] has a water-like hydrogen bond network [1–7], but in contrast to water, hydrogen bonds of ethylene glycol are both inter- and intramolecular. Formation of the weaker intramolecular H-bonds in liquid EG [1,2] results in decrease of H-bonds number per one molecule in comparison with that for water [2,3,5,7,25–27]. Thus, assumed tetrahedral structure of EG will be defective due to existing of -CH_2-CH_2- grouping. In EG molecule, the number of weakly polar methylene groups is equal to the number of hydroxyl groups. This means that hydrogen bonding will have a considerable influence on EG properties.

tert-Butanol (TBA) ($\varepsilon = 10.9$, $\mu = 1.66$ D, $\eta = 3.316$ mPa·s at 303 K; $T_{\text{melting}} = 298.65$ K; $T_{\text{boiling}} = 355.35$ K) [23,24] includes three hydrophobic $-CH_3$ and one hydrophilic $-OH$ groups. Hydrophobic groups display solvophobic effects which result in strengthening of interactions between solvent molecules in solvation shell, whereas polar hydroxyl is able to form strong hydrogen bonds with molecules of both EG and TBA.

Information on volume properties of EG–TBA binary mixture is absent in literature, although the individual solvents have been extensively studied. In this connection, mixtures of these solvents over the wide range of state parameters are of interest. This work is a continuation of our previous investigations devoted to study of volume properties of binary systems as function of composition, temperature and pressure [28–35].

2. Experimental

Ethylene glycol (purity 99.8 %) and *tert*-butanol (purity 99.3 %) were purified by double distillation according to references [36,37] and were kept under vacuum. Water content was determined with K. Fisher method and it did not exceed 0.02 wt.% (or $0.6 \cdot 10^{-5}$ mole fraction) for EG and 0.015 wt.% (or $4 \cdot 10^{-5}$ mole fraction) for TBA.

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Mixtures were prepared gravimetrically from the degassed solvents without contact of the solution with atmospheric air. Freshly prepared solutions were used for the measurements, and the densimeter was self-flowing filled from the sealed reservoir. For all stages of density measurements drying column with calcined silica gel was used. Mixtures under consideration were permanently stirred under measurements.

Densities (ρ) were determined using Anton-Paar DMA 4500 vibrating tube densimeter. It was equipped with built-in thermostat with two platinum thermometers (Pt 100), due to which the temperature was held constant (± 0.005 K). Densimeter was daily calibrated by twice-distilled water and dry air. Measurements were performed over the temperature range of 278.15–348.15 K. Densities were not measured in the whole composition range at 278.15, 288.15 and 298.15 K due to mixture freezing.

The uncertainties of mixture preparation and temperature measurements were less than $2 \cdot 10^{-5}$ mole fraction and 0.01 K, respectively. Reproducibility and the total uncertainty of density measurements were $1 \cdot 10^{-5}$ and $5 \cdot 10^{-5}$ g/cm^3, respectively.

In Table 1 the comparison of our data on densities of pure ethylene glycol and *tert*-butanol with literature ones is presented. Our results are in a very good agreement with data by Afzal et al. [38] over the whole temperature range (the deviation is less than $+0.01\%$) and with data by Sakurai [39] (the deviation is about -0.05%), but relative deviation from values obtained by Geyer et al. [40] is of $+0.10 \div 0.15\%$. The maximum of relative deviation of *tert*-butanol densities over temperature range of 303–323 K, with the largest number of experimental points, changes from $+0.025\%$ to 0.09%, and is equal to -0.21% (results by Harris et al. [41]) at 348.15 K. Very good accordance is observed between our data and ones by Kim and Marsh [42] and by Martinez et al. [43]. Whereas with temperature increasing the relative deviation of densities from results by Kim and Marsh [42] decreases, the deviation from results by Nain [44] increases.

Experimental densities of ethylene glycol + *tert*-butanol mixtures over the temperature range of 274.15–348.15 K at atmospheric pressure are summarized in Table 2.

3. Calculations and results

Excess molar volume V_m^E is determined by equation:

$$V_m^E = V_m - x_1 V_1^o - x_2 V_2^o \tag{1}$$

where V_m is the molar volume of mixture; V_1^0, x_1, and V_2^o, x_2 are molar volumes of pure components and its mole fraction, respectively.V_m^E values were calculated directly from the experimental data using the following expression:

$$V_m^E = x_1 M_1 (1/\rho - 1/\rho_1) + x_2 M_2 (1/\rho - 1/\rho_2) \tag{2}$$

where M_1, ρ_1 and M_2, ρ_2 are molar masses and densities of ethylene glycol and *tert*-butanol, respectively; ρ is density of the mixture. The uncertainty of determination of excess molar volumes was within ± 0.03 cm^3/mol.

Values of excess molar volumes V_m^E were described by Redlich–Kister equation [45]:

$$V_m^E = x_2 (1 - x_2) \sum_{i=0}^{i=n} A_i (1 - 2x_2)^i. \tag{3}$$

To analyze the intermolecular interactions at low components concentrations dependences of $V^E / x_1 x_2$ were considered [46]. As the result demonstrated there were specific interactions in the mixture at low *tert*-butanol content.

The appropriate degree n of Eq. (3) was determined by standard deviation σ being calculated as:

$$\sigma = \left[\sum \left(V_{\text{exp}}^E - V_{\text{cal}}^E \right)^2 / (N - (n+1)) \right]^{1/2} \tag{4}$$

where N is the total number of experimental points; $(n+1)$ is a number of coefficients (A_i) in Eq. (3). Calculated values of A_i and σ at every temperature are reported in Table 3.

Apparent molar volumes of ethylene glycol $V_{\phi 1}$ and apparent molar volumes of *tert*-butanol $V_{\phi 2}$ for each isotherm were evaluated from the experimental data with relations Eqs. (5)–(6):

$$V_{\phi 1} = \frac{(V_m - x_2 V_2^o)}{x_1} = \frac{(\rho_2 - \rho) x_2 M_2}{x_1 \rho \rho_2} + \frac{M_1}{\rho} \tag{5}$$

$$V_{\phi 2} = \frac{\left(V_m - x_1 V_1^0\right)}{x_2} = \frac{(\rho_1 - \rho) x_1 M_1}{x_2 \rho \rho_1} + \frac{M_2}{\rho}. \tag{6}$$

Partial molar volumes of components $\bar{V}_1$ and $\bar{V}_2$ were calculated as follows:

$$\bar{V}_1 = V_m - x_2 (\partial V_m / \partial x_2) = M_1 (1/\rho - w_2 \partial (1/\rho) / \partial w_2) \tag{7}$$

$$\bar{V}_2 = V_m - x_1 (\partial V_m / \partial x_1) = M_2 (1/\rho - w_1 \partial (1/\rho) / \partial w_1) \tag{8}$$

where w_i is a mass fraction of the i-component in the mixture. To calculate the partial molar volumes $(\partial (1/\rho) / \partial w_i)$ dependences were described by the 6-th order polynomial and differentiated.

Partial molar volumes also were calculated by differentiation of Eq. (3) on x_2 and combination of differentiation results with Eqs. (9) and (10):

$$\bar{V}_1 = V_1^o + V_m^E - x_2 \left(\partial V_m^E / \partial x_2 \right) \tag{9}$$

Table 1
The experimental and literature data on the density values of pure ethylene glycol and *tert*-butanol at atmospheric pressure.

Solvent	T/K	$\rho/(\text{g} \cdot \text{cm}^{-3})$	
		Experimental	Literature
Ethylene glycol	278.15	1.12377	1.12371 [38], 1.124265 [39], 1.1222 [40], 1.123664 [62]
	288.15	1.11683	1.11676 [38], 1.117244 [39], 1.1156 [40], 1.116906 [62], 1.11674 [63]
	298.15	1.10983	1.10977 [38], 1.110212 [39], 1.1086 [40], 1.109913 [62], 1.11006 [63], 1.1099 (298.2 K) [64], 1.10988 [66]
	308.15	1.10281	1.10272 [38], 1.103164 [39], 1.1019 [40], 1.103089 [62], 1.10288 [63], 1.10282 [65], 1.10289 [66]
	323.15	1.09212	1.09202 [38], 1.092946 [62], 1.0923 (323.2 K) [64], 1.09105 [65]
	333.15	1.08490	1.08478 [38]
	348.15	1.07384	1.07370 (348.14 K) [38]
tert-Butanol	308.15	0.77015	0.77008 [17], 0.76997 [42], 0.77020 [43], 0.77039 [44]
	323.15	0.75394	0.75448 при 323.14 K [18], 0.75401 [42], 0.7541 [67]
	333.15	0.74270	
	348.15	0.72506	0.725824 при 348.13 K [41], 0.7266 [67]