



Volume effects for binary mixtures of propane-1,2-diol with methanol, propan-1-ol, hexan-1-ol, octan-1-ol, or nonan-1-ol at temperatures (293.15 to 318.15) K

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ABSTRACT

Values of the density for binary mixtures of propane-1,2-diol with methanol, propan-1-ol, hexan-1-ol, octan-1-ol, or nonan-1-ol were measured over the entire composition range and within the temperature range from (293.15 to 318.15) K by means of a vibrating tube densimeter. The excess molar volumes and limiting excess partial molar volumes were calculated. The Redlich–Kister polynomials were fitted to the results and smooth representations of the results are presented. The negative values of the excess molar volumes over the entire composition and temperature ranges are observed in the case of methanol and propan-1-ol. In the cases of hexan-1-ol, octan-1-ol, and nonan-1-ol, positive values of the excess molar volumes over the entire composition and temperature ranges are observed. The effect of temperature is discussed qualitatively.

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1. Introduction

Binary systems of highly associated hydroxyl compounds are an important and very interesting class of solutions both from practical and theoretical point of view. Unfortunately, their properties are still not properly understood because interpretation of the mixing effects is extremely difficult (various possible interactions and size effects). At the same time, there is a lack of suitable tools based on statistical mechanics for description of properties with a comparable quality as for non-associating liquid mixtures. Very interesting are systems with bi-functional compounds, e.g., an alkanediol, all the more because the pure diols themselves are interesting compounds due to the possibility of formation both inter- and intramolecular hydrogen bonding. Systematic studies of mixing phenomena in associated binary systems of alkanediol with alkan-1-ol have been undertaken in our lab many years ago. Recent papers have reported among others properties of ethane-1,2-diol with butan-1-ol, hexan-1-ol, or octan-1-ol [1,2], ethane-1,2-diol with pentan-1-ol [3,4], ethane-1,2-diol with nonan-1-ol [5], and butane-1,4-diol with butan-1-ol [6]. The aim of this work is to study the composition dependence of volume effects for binary mixtures of propane-1,2-diol with methanol, propan-1-ol, hexan-1-ol, octan-1-ol, or nonan-1-ol as a function of composition and temperature.

A survey of the literature shows that some volumetric data for the mixtures under test have been reported [7–13] previously. In the case of mixtures of propane-1,2-diol with methanol, three data sets of excess molar volumes have been found, e.g., Lee [7] and

Zarei *et al.* [8] reported results at temperatures (283.15, 293.15, and 303.15) K and (298.15, 303.15 and 308.15) K, respectively, whereas Orge *et al.* [9] reported only isothermal data at $T = 298.15$ K. Unfortunately, the agreement between the above data is not satisfactory. In another paper of Zarei *et al.* [10], results for mixtures of propane-1,2-diol with propan-1-ol over the temperature range from (293.15 to 343.15) K are reported. For this system, isothermal (298.15 K) data are also reported by Pal *et al.* [11] and by Garcia and Paz-Andrade [12]. Unfortunately, here disagreement is also observed. Mixtures of propane-1,2-diol with hexan-1-ol have been investigated at temperatures (298.15, 303.15 and 308.15) K by Doghaei *et al.* [13] and at temperature 298.15 K by Garcia and Paz-Andrade [12]. Unfortunately, the agreement between the excess molar volumes reported in the above papers is also not satisfactory (at equimolar composition the V^E values at $T = 298.15$ K are $(0.313 \cdot 10^{-6}$ and $0.255 \cdot 10^{-6})$ $\text{m}^3 \cdot \text{mol}^{-1}$, respectively). Thus, generally, consistency of data from different sources is unsatisfactory and it is not known which one are correct. Simultaneously, to the best of our knowledge, there are no experimental values with regard to mixtures of propane-1,2-diol with octan-1-ol or nonan-1-ol. This situation has prompted us to more systematic investigation of the volume effects as function of temperature within the range from (293.15 to 318.15) K.

2. Experimental

The sources and purity of chemical samples are listed in table 1. All chemicals were used as supplied without further purification.

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TABLE 1
Provenance and purity of the materials.

Chemical name	Source	Mass fraction purity	Mass fraction of water ^a
Propane-1,2-diol	Sigma-Aldrich	0.995	$<1 \cdot 10^{-3}$
Methanol ^b	Fluka	0.995	$\leq 1 \cdot 10^{-4}$
Propan-1-ol ^c	Sigma-Aldrich	0.999	$\leq 5 \cdot 10^{-4}$
Hexan-1-ol ^d	Aldrich	0.99+	$\leq 5 \cdot 10^{-5}$
Octan-1-ol ^e	Aldrich	0.99+	$\leq 1 \cdot 10^{-4}$
Nonan-1-ol	Alfa-Aesar	0.99	$<1 \cdot 10^{-3}$

^a Determined by Karl Fisher method.^b Absolute over molecular sieves, stored under argon.^c Chromasolv.^d Anhydrous, Sure/Seal, stored under nitrogen.^e For HPLC.

In the case of propane-1,2-diol, various samples from the same source were used. The purities of the alcohols were checked also by comparing measured densities with those reported in the literature (see table 2). Most of the data show satisfactory agreement.

Solutions (tens of grams) were prepared by mass (precision $\pm 1 \cdot 10^{-6}$ kg) and stored before measurement no more than a few hours in sealed flasks. The uncertainty of the determination for the mole fraction was estimated to be of $\pm 5 \cdot 10^{-5}$.

The densities were measured with a vibrating-tube densimeter DMA 5000 (Anton Paar, Austria), provided with automatic viscosity correction. The densimeter was calibrated using the air and water as standards. The water was re-distilled, deionized, and degassed by boiling. Its electrolytic conductivity was $1 \cdot 10^{-4} \text{ S} \cdot \text{m}^{-1}$. Before the density measurements, the samples were degassed using high amplitude ultrasound. The expected uncertainty and repeatability of the measured densities are ($\pm 5 \cdot 10^{-2}$ and $\pm 5 \cdot 10^{-3}$) $\text{kg} \cdot \text{m}^{-3}$, respectively.

The temperatures are reported in terms of ITS-90. The molar values are reported in terms of the 1996 IUPAC relative atomic masses [24].

3. Results and discussion

Experimental densities, ρ , of binary mixtures of propane-1,2-diol with methanol, propan-1-ol, hexan-1-ol, octan-1-ol, or nonan-1-ol measured over the entire composition range and at the temperatures from (293.15 to 318.15) K are summarized in table 3. Because in the present study, various samples of propane-1,2-diol were used, the average density has been calculated. The average value at $T = 298.15 \text{ K}$ is equal to (1032.526 \pm

0.018) $\text{kg} \cdot \text{m}^{-3}$. Taking into account declared uncertainties, the consistency is very satisfactory. The values of the excess molar volumes V^E were determined from the equation:

$$V^E = V - \sum_{i=1}^2 x_i V_i, \quad (1)$$

where V is the molar volume, x_i is the mole fraction of component i of the system, and V_i is the molar volume of component i of the system.

Each set of values of V^E was fitted to the Redlich–Kister type equation:

$$V^E(\text{m}^3 \cdot \text{mol}^{-1}) = x_1 \cdot (1 - x_1) \cdot \sum_{i=1}^n a_i \cdot (1 - 2x_1)^{i-1}, \quad (2)$$

where x_1 is the mole fraction of the first component, *i.e.*, propane-1,2-diol. Values of the coefficients a_i , determined by the least-squares analysis, are listed in table 4 where standard deviations δ from regression lines are also given. The optimum number of the coefficients was ascertained from an examination of the δ and all experimentally values were equally weighted. The corresponding values of V^E are reported in table S1 of the Supporting information.

The results are shown in figures 1–5. For clarity, in most cases only results at three temperatures (298.15, 308.15, and 318.15) K are presented. It appears that the mixtures of propane-1,2-diol with two lower alkan-1-ols investigated (figures 1 and 2), *i.e.*, methanol and propan-1-ol shown contraction of volume ($V^E < 0$), *i.e.*, the packing of the molecules in mixtures is more compact than that in the pure components. In other words, the methanol and propan-1-ol can readily be incorporated into the structure of propane-1,2-diol and vice versa. In the case of methanol, the $V^E(x_1)$ curves are asymmetrical with minimum at mole fraction of propane-1,2-diol $x_1 \approx 0.4$. The agreement between results obtained in this work, those of Zarei *et al.* [8], and those of Orge *et al.* [9] is excellent. On the other hand, the agreement with data of Lee [7] is poor. This may arise from a number of factors. Zarei *et al.* [8] supposed that such significant discrepancy with the data of Lee [7] can be related to viscosity correction. It is worth noting here that analysis of the data of Lee shows that the effect of temperature on molar volume is indistinct (although the measurements were made with 10 K steps). In the case of mixtures of propane-1,2-diol with propan-1-ol, the comparison with literature values reveals that the data here are generally rather not consistent (figure 2). Both the V^E values of Garcia and Paz Andrade [12] and values of Pal *et al.* [11] are less negative than those obtained in this work. At the same time the V^E values reported by Zarei *et al.* [10] are

TABLE 2
Values of density, ρ , of pure compounds compared with the selected literature data at $T = 298.15 \text{ K}$.

Property	Exptl.	Lit.	AAD ^b
$\rho/\text{kg} \cdot \text{m}^{-3}$	1032.526 ^c	<i>Propane-1,2-diol</i>	
		1032.5 [9], 1032.22 [14], 1032.55 [15], 1032.61 [8,10], 1032.7 [12], 1032.77 [16], 1032.8 [17], 1032.86 [18], 1033.1 [13]	
$\rho/\text{kg} \cdot \text{m}^{-3}$	786.794	<i>Methanol</i>	
		786.6 [9], 786.57 [8], 786.548 [19], 786.61 [20], 786.573 [21], 786.37 [17]	
$\rho/\text{kg} \cdot \text{m}^{-3}$	799.528	<i>Propan-1-ol</i>	
		799.49 [10], 799.666 [19], 799.57 [20], 799.572 [21], 799.60 [17]	
$\rho/\text{kg} \cdot \text{m}^{-3}$	815.188	<i>Hexan-1-ol</i>	
		815.4 [13], 815.28 [1], 815.34 [17], 815.37 [20], 815.230 [22]	
$\rho/\text{kg} \cdot \text{m}^{-3}$	821.647	<i>Octan-1-ol</i>	
		821.75 [1], 821.57 [17], 821.79 [20], 821.826 [22]	
$\rho/\text{kg} \cdot \text{m}^{-3}$	824.254	<i>Nonan-1-ol</i>	
		824.48 [5], 824.238 [23], 824.455 [22]	

^a Standard uncertainty $u(\rho/\text{kg} \cdot \text{m}^{-3}) = 0.05$.^b Average absolute deviation (percent).^c Mean value.

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