



Thermodynamic and acoustic properties of binary mixtures of 1-butanol with 1,2-butanediol. The comparison with the results for 1,3-, and 1,4-butanediol



Edward Zorębski^{a,*}, Paweł Góralski^b, Bożena Godula^a, Michał Zorębski^a

^a Institute of Chemistry, Silesian University, Szkolna 9, 40-006 Katowice, Poland

^b Department of Physical Chemistry, University of Łódź, Pomorska 165, 90-236 Łódź, Poland

ARTICLE INFO

Article history:

Received 10 June 2013

Received in revised form 5 August 2013

Accepted 31 August 2013

Available online 11 September 2013

Keywords:

Density

Heat capacity

Speed of sound

Compressibility

Excess

Alcohols

ABSTRACT

Densities and isobaric heat capacities have been measured for (1-butanol + 1,2-butanediol) over the temperature range from (293.15 to 308.15) K and (282.15 to 320.15) K, respectively. The speed of sound at the temperature 298.15 K has been measured as well. Using these results, the molar volumes, isentropic and isothermal compressibility coefficients, molar isentropic and isothermal compressibilities, molar isobaric and isochoric heat capacities as well as internal pressures were calculated. Also the corresponding excess and deviation values were calculated and expressed by Redlich–Kister polynomials. The results are discussed in terms of variations of the structure of the system caused by the participation of the two alcohols (with the same carbon chain but different hydroxyl groups) in the dynamic intermolecular association process through hydrogen bonding at various temperatures. Present findings are also compared with the previous results for 1,3-, and 1,4-butanediol.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

This work presents the next part of a continuing study of binary mixtures of 1-butanol with isomeric butanediols aimed at gaining a better understanding of association (the nature and dynamics of alcohol structures) in these hydrogen-bonded systems [1–7]. Most interesting is the examination of the effect of the placement of hydroxyl groups in the isomeric butanediol molecules on the physicochemical properties of above-mentioned systems. To this end, we report this time the results of our volumetric, calorimetric, and acoustic investigations of (1-butanol + 1,2-butanediol) within the temperature range from (293.15 to 308.15) K, (282.15 to 320.15) K, and at $T = 298.15$ K, respectively. For the system under study, some properties were determined in our lab previously. However, these preliminary results are reported only in a graphical form (volume effect, isentropic compressibilities, and ultrasonic absorption coefficients at $T = 298.15$ K [3]). As far as we know, no heat capacity data have been reported in the literature for the system studied.

2. Experimental

2.1. Chemicals and materials

The chemicals were used without further purification. However, the water content was determined by the Karl Fischer method. In this work, samples used for acoustic and volumetric experiments were other than those for the calorimetric experiment. In the case of 1-butanol for samples from various suppliers within experimental errors, no differences in checked parameters were observed. In the case of 1,2-butanediol samples from various suppliers were used as well. Details about suppliers and purity are given in table 1.

All mixtures were prepared by mass (uncertainty $\pm 6 \cdot 10^{-7}$ kg) using analytical balances. The uncertainty of the mole fraction was estimated to be not worse than $\pm 5 \cdot 10^{-5}$. Before all measurements, each sample was degassed. The ultrasonic cleaner (Unitra-Unima UH4, $f = 25$ kHz, 15 min) was used.

2.2. Apparatus and procedures

The densities were measured with two *ca.* 30 cm³ bicapillary pycnometers. The pycnometers were held during measurements in a water thermostat at constant T (better than ± 0.01 K). The liquid level in each capillary (*ca.* 0.1 m in length) was measured using a precise vertical cathetometer. The pycnometers were

* Corresponding author.

E-mail address: emz@ich.us.edu.pl (E. Zorębski).

TABLE 1
Sample table.

Chemical name	Acronym	Source	Purity ^a	Water content ^{a,b}
1-butanol ^c	1BU	Fluka	>0.995	$9.7 \cdot 10^{-4}$
1-butanol ^d		Merck	>0.995	$3.7 \cdot 10^{-4}$
1,2-butanediol ^c	1,2BD	Fluka	>0.99	$7.8 \cdot 10^{-4}$
1,2-butanediol ^d		Aldrich	>0.990	$4.0 \cdot 10^{-4}$

^a Mass fraction.^b Karl Fisher method.^c Acoustic and volumetric experiment.^d Calorimetric experiment.

calibrated using deionised and degassed (as above) water. Its electrolytic conductivity was $1.3 \cdot 10^{-4} \text{ S} \cdot \text{m}^{-1}$. As standard values, the densities of water calculated by Kell's equation [8] were used. In the calculations of density for the buoyancy correction, the air density for ambient temperature and barometric pressure was used. The expected uncertainty of the measured densities is $\pm 5 \cdot 10^{-2} \text{ kg} \cdot \text{m}^{-3}$ while the repeatability is $\pm 5 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$. More details concerning the density measurements can be found in the paper of Ernst et al. [9].

Isobaric heat capacities were measured by means of a differential scanning calorimeter Micro DSC III from Setaram. Details of the procedure applied and the calorimeter calibration can be found elsewhere [10]. In our case, the uncertainty of the measurements was estimated to be about $\pm 0.5\%$.

The speed of sound was measured by a pulse-echo-overlap method (its advantages and disadvantages have been previously described [11]) with a measuring set (OPE-4F) designed and constructed in our laboratory [12]. The cell calibration was made by the use of water as a reference liquid and the value of the speed of sound in water reported in [13] was used. Water (electrolytic conductivity $1.2 \cdot 10^{-4} \text{ S} \cdot \text{m}^{-1}$) was prepared as for density measurements. The temperature stabilization ($\pm 5 \cdot 10^{-3} \text{ K}$) was realized by means of two thermostats in a cascade arrangement and a temperature controller (PI type, Unipan 660, Poland). The repeatability of the speed of sound measurements was estimated to be better than $\pm 0.1 \text{ m} \cdot \text{s}^{-1}$. The uncertainty was estimated to be of the order of $\pm 0.5 \text{ m} \cdot \text{s}^{-1}$. More details can be found in previous papers [12,14].

Reliability of the measurements reported in this work is checked also by comparing measured values of density ρ , speeds of sound u , refractive index n_D , and molar isobaric heat capacity $C_{p,m}$ with those reported in the literature (table 2). Generally, good agreement was found between the measured and literature values.

All calculations of the molar values reported in this work are based on the 1996 IUPAC relative atomic masses [25]. The temperatures are reported according to ITS-90.

3. Results and discussion

3.1. Data processing

All experimental values of $C_{p,m}$ obtained for pure compounds and mixtures within the investigated temperature range (each time ca. 2000 recorded experimental points) were approximated by the polynomials in the form:

$$C_{p,m}(T) = \sum_{i=1}^3 a_i \cdot (T/(100 \cdot \text{K}))^{i-1}, \quad (1)$$

where a_i are the fitting coefficients, and T is the temperature. It should be stressed that the above equation is excellent for interpolation and dividing T by the factor of 100 improves the numerical stability. The a_i coefficients estimated by an unweighted least-squares method and the standard deviations from the regression lines δ are reported in table S1 of the Supporting Information (SI). We note that the residual values of the above fit are small and the values calculated from the obtained regression functions are equal to the raw data within the limits of the measurement uncertainty. In this work for each sample, two experiments were conducted, i.e., with the increasing and decreasing temperature scan. The averaged isobaric molar heat capacities $C_{p,m}$ for pure compounds are presented in table 4 with the 5 K step.

In this work, all obtained excess and deviations values are fitted by the polynomials of the Redlich–Kister type

$$Y^E = x \cdot (1-x) \cdot \sum_{i=1}^n a_i \cdot (1-2 \cdot x)^{i-1}, \quad (2)$$

where x is the mole fraction of 1,2BD, a_i are parameters estimated by the unweighted least-squares method, and Y^E is the excess or deviations property. The optimum number of the coefficients was ascertained from an examination of the standard deviation δ . Note that all excesses were calculated from the relation:

$$Y^E(x, T) = Y(x, T) - Y^{id}(x, T), \quad (3)$$

where Y and Y^{id} denote thermodynamic property in real and ideal mixture, respectively, and all three terms, as indicated, refer to the same temperature and composition.

3.2. Volume effects

Using experimental densities reported in table 3, the excess molar volumes V^E (collected in table S2) were calculated by the use of equation (3). The molar volumes for ideal mixtures V^{id} were calculated as the mole fraction averaging of the molar volume of the

TABLE 2
Densities ρ speeds of sound u , isobaric heat capacities $C_{p,m}$, and refractive indices n_D of pure components together with literature data at $T = 298.15 \text{ K}$.

Property	This work	Lit.
		<i>1,2-butanediol</i>
$\rho/\text{kg} \cdot \text{m}^{-3}$	998.59 ^a	998.408 [15], 998.86(1) [16], 998.87 [17] 999.00 [18], 998.1 [19]
$u/\text{m} \cdot \text{s}^{-1}$	1449.92	1451.16 [15], 1452.0 [16], 1453.0 [17]
$C_{p,m}/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	231.06 ^b	230.94 [5], 228.8 [17]
n_D	1.4364 ^c	1.4370 [15]
		<i>1-butanol</i>
$\rho/\text{kg} \cdot \text{m}^{-3}$	805.81 ^a	805.77 [7], 805.75 [20], 805.737 [22], 805.83 [23]
$u/\text{m} \cdot \text{s}^{-1}$	1240.25	1239.39 [7,23], 1240.0 [22], 1240.5 ^d [24]
$C_{p,m}/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	176.90 ^b	177.10 [5], 177.16 [21], 176.83 [4]
n_D	1.3972 ^c	1.39741 [20]

^a Acoustic and volumetric experiment.^b Mean value from two experiments: increasing and decreasing temperature scan.^c PZO RL2 Abbe refractometer, uncertainty ± 0.0002 .^d Mean value ($\pm 1.2 \text{ m} \cdot \text{s}^{-1}$) calculated from various literature data.

Download English Version:

<https://daneshyari.com/en/article/215580>

Download Persian Version:

<https://daneshyari.com/article/215580>

[Daneshyari.com](https://daneshyari.com)