J. Chem. Thermodynamics 92 (2016) 97–107

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

# FT-IR spectroscopic study of excess thermodynamic properties of liquid mixtures containing benzylalcohol with alkoxyalkanols

M. Raveendra [a], C. Narasimharao [b], L. Venkatramana [c], K. Sivakumar [d,*], K. Dayananda Reddy [a]

[a] Department of Chemistry, P.V.K.N.Govt. Degree & P.G. College, Chittoor 517001, A.P., India
[b] Department of Chemistry, S.V. University, Tirupati 517502, A.P., India
[c] Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India
[d] Department of Chemistry, S.V.Arts Degree & P.G.College (T.T.D'S), Tirupati 517502, A.P., India

ARTICLE INFO

*Article history:*
Received 9 July 2015
Received in revised form 30 August 2015
Accepted 31 August 2015
Available online 5 September 2015

*Keywords:*
Intermolecular interaction
Redlich–Kister equation
FT-IR spectrum
Binary mixture

ABSTRACT

Densities ($\rho$) of pure liquids and their mixtures have been measured at $T$ = 298.15 K to $T$ = 318.15 K and 0.1 MPa pressure over the entire composition range for the binary mixtures of benzylalcohol (BA) with 2-Methoxyethanol (ME), 2-Ethoxyethanol (EE), 2-Butoxyethanol (BE) by using Rudolph Research Analytical digital densitometer (DDH-2911 model). Further, the speed of sound ($u$) for the above said mixtures was also measured at $T$ = 298.15 K and $T$ = 308.15 K. Values of the experimental density were used to calculate the excess volumes ($V^E$), in turn were compared with Redlich–Kister and Hwang equations. Isentropic compressibility ($\kappa_S$) and excess isentropic compressibility ($\kappa_S^E$) were evaluated from experimental speed of sound and density data. Moreover, the experimental speed of sound was analysed in terms of theoretical models, namely Schaaff's collision factor theory (CFT) and Jacobson's free length theory (FLT). The experimental results are discussed in terms of intermolecular interactions between component molecules of binary mixtures and also FT-IR Spectroscopic studies.



## 1. Introduction

Thermodynamic properties of mixtures which contain a blend of organic solvents with alkoxyalkanols are important from the technological and theoretical points of view. Further, it is well known that the study of excess thermodynamic properties like excess volume, excess isentropic compressibility is much important to understand the molecular interactions in liquid mixtures and develop and test the solution theories and mathematical models [1]. The selection of the systems in the present investigation has a variety of applications not only on the molecular structure of the industrial components but also their industrial and ecological importance. The liquid components that are selected as binary mixtures, in the present investigation are well known organic liquids; they are chosen and also have wide range of applications in various fields of chemistry besides being used in industries and routine analytical work. Benzylalcohol is used as versatility of a solvent for gelatin, cellulose acetate, shellac and for pharmaceutical aid as an antimicrobial agent [2]. It is also used in perfumery, in microscopy as an embedding material, and in veterinary applications [3]. Alkoxyalkanols are oxygenated compounds are increasingly used as additives to gasoline due their octane enhancing and pollution reducing properties [4,5]. Moreover, hydroxyl ethers are non-ionic amphiphile molecule, very effective as surfactants with a large number of applications [6,7]. Moreover, 2-alkoxyalkanols are a very interesting class of solvent having ether *i.e.* oxygen (–O–) or hydroxyl (–OH) group and is noted for its donating and accepting ability. In this article an investigation was undertaken of the systems containing the binary mixtures of benzylalcohol and alkoxyalkanols, which makes the possible study of self-association via inter and intra molecular hydrogen bonding through the –OH (Hydroxyl) and –O– (ether) groups in the same molecule. [8–11]. In the present study an attempt has been made to provide insight into the nature of molecular interactions occurring between benzylalcohol and alkoxyalkanols by measuring the densities ($\rho$) at $T$ = 298.15 K to $T$ = 318.15 K and speeds of sound ($u$) at $T$ = 298.15 K and $T$ = 308.15 K. Further, the present work will provide that an increasing chain length of alkoxyalkanols from methoxy to butoxy may influence both the sign and magnitude of excess thermodynamic functions. Moreover, the measured values of the speed of sound are also analysed in terms of Schaaff's collision factor theory (CFT) [12] and Jacobson's free length theory (FLT) [13,14]. FT-IR Spectroscopic data are also collected in the present investigation to learn of the existence of intermolecular hydrogen bonding between benzylalcohol and alkoxyalkanol molecules.

* Corresponding author. Tel.: +91 9290080843.
*E-mail address:* sivakumarkasi64@gmail.com (K. Sivakumar).

http://dx.doi.org/10.1016/j.jct.2015.08.040
0021-9614/

## 2. Experimental

### 2.1. Materials

All the chemicals (A.R. grade) were used in the present work supplied by S.D.Fine Chem. Ltd., India. The mass fraction purity of all the chemicals is as follows: benzyl alcohol (>0.99), 2-methoxyethanol (>0.99), 2-ethoxyethanol (>0.98), and 2-butoxyethanol (0.99). Alkoxyalkanols were further purified by the methods as described in the literature previously [15–17]. The prior to experimental measurements of all liquid samples were stored in a dry-box over phosphorous pentoxide to reduce the water content and partially degassed by ultrasound. The mass fraction purity of the purified liquids as determined by gas chromatography is as follows: benzylalcohol (0.996), 2-methoxyethanol (0.993), 2-ethoxyethanol (0.987), and 2-butoxyethanol (0.994). Moreover, name of the chemical, source, CAS number, purity in mass fraction and water content of the component liquids are given in table 1.

### 2.2. Measurements

The water content of solvents used in this work was measured by Analab (Micro Aqua Cal 100) Karl Fischer Titrator and Karl Fisher reagent from Merck. It can detect water content from less than $10 \cdot 10^{-6}$ to 100% by conductometric titration with dual platinum electrode.

All the binary liquid mixtures were prepared by weighing an appropriate amount of pure liquids on an electronic balance (Afoset, ER –120A, India) with a precision of ±0.1 mg by syringing each component into airtight stopper bottles to minimize the evaporation and moisture content. The uncertainty of the mole fraction was $\pm 1 \cdot 10^{-4}$. After mixing the sample, the bubble free homogenous sample was transferred into the U-tube of the densimeter through a syringe. The density measurements were performed with a Rudolph Research Analytical digital densimeter (DDH-2911 Model), equipped with a built-in solid-state thermostat and a resident program with accuracy of temperature of (298.15 K ± 0.03) K. The uncertainty of density measurement liquid mixtures is $\pm 2 \cdot 10^{-3}$ g · cm$^{-3}$ and the uncertainty of temperature ±0.01 K, Proper calibrations at each temperature were achieved with doubly distilled, deionised water and with air as standards. A multi frequency ultrasonic interferometer (M-82 Model, Mittal Enterprise, New Delhi, India) operated at 2 MHz, is used to measure the speed of sound, of the binary liquid mixtures at $T$ = 298.15 K and $T$ = 308.15 K by using a digital constant temperature water bath. The uncertainty in the measurement of speed of sound is ±0.3% and the uncertainty of temperature ±0.02 K. The temperature stability was maintained within ±0.01 K by circulating thermostatic water bath around the cell with a circulating pump. In order to minimize the uncertainty of the measurement, several maxima were allowed to pass and their number (50) in the present study was counted. All maxima are recorded with the highest swing of the needle on the micrometre scale. The total distance $d$ (cm) moved by the reflector is given by $d = n\lambda/2$, where $\lambda$ is the wave length. The frequency, $\nu$, of the crystal being accurately known (2.0 MHz), the speed of sound, $u$ in ms$^{-1}$ is calculated by using the relation $u = \nu\lambda$. The details of its calibration, the experimental setup and measuring procedure have been described previously [18]. The working of the interferometer was tested by comparing the measured speed of sound of pure samples of benzylalcohol and 2- alkoxyalkanols, which are in good agreement with literature values [19–40] at the studied temperatures and are reported in table 2. FTIR spectra have been measured by an ALPHA FT-IR Spectrometer (Bruker) to study the existence of intermolecular hydrogen bonding between benzylalcohol and 2-alkoxyalkanols.

## 3. Results and discussion

### 3.1. Excess volumes ($V^E$)

The non-ideal behaviour between binary mixtures of benzylalcohol and 2-alkoxyalkanols were represented in terms of excess molar volume $V^E$ , which is computed from the experimentally determined density using following equation

$$V_E/\mathrm{cm}^2 \cdot \mathrm{mol}^{-1} = [(X_1M_1 + X_2M_2)/\rho_m - (X_1M_1/\rho_1 + X_2M_2/\rho_2)], \quad (1)$$

where, $X_i$ is the mole fraction of component $i(i = 1,2)$ in the mixture; $M_i$ is the molar mass; $\rho_m$ and $\rho_i$ are the measured density of the mixture and the pure component $i(i = 1,2)$ respectively. Further, the $V^E$ values are also graphically represented in figure 1 at $T$ = 298.15 K for all mixtures. The calculated $V^E$ values were fitted to Redlich–Kister [41] and Hwang *et al.* [42] equations and these are given in table 3. The methods and calculation of $V^E$ in terms of Hwang equation were described earlier [43,44].

The Redlich–Kister equation is:

$$V_E/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1} = X_1(1 - X_1)\left[a_0 + a_1(2X_1 - 1) + a_2(2X_1 - 1)^2\right]. \quad (2)$$

The Hwang *et al.* equation is:

$$V^E/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1} = X_1X_2[b_0 + b_1X_1^3 + b_2X_2^3], \quad (3)$$

where $a_0$, $a_1$ and $a_2$ and $b_0$, $b_1$ and $b_2$ are adjustable parameters and $X_1$ is the mole fraction of benzylalcohol. The values of parameters were obtained by the least-square method and these values of the parameters are given in table 4.

An examination of $V^E$ values in figure 1 shows that negative values are present at all temperatures over the entire composition for binary mixtures of benzylalcohol with 2-alkoxyalkanols. The sign of the excess molar volume $V^E$ of the system depends on the relative magnitude of expansion and contraction of mixing two liquids [45–52]. The values of $V^E$ become more negative as the length of the alkyl chain length of the alkoxyalkanols molecules decreases (figure 2) and show the following effects.

**TABLE 1**
Name of the chemical, source, CAS number, purity in mass fraction, purity analysis method and water content in mass fraction of the chemicals used in this work.

| Component | Source | CAS number | Purity in mass fraction (as received from supplier) | Purity in mass fraction (after purification) | *Analysis method | Water content in mass fraction |
|---|---|---|---|---|---|---|
| Benzylalcohol | S.D.Fine Chem. Ltd. | 100-51-6 | 0.99 | 0.996 | GC | 0.0005 |
| 2-Methoxyethanol | S.D.Fine Chem. Ltd | 109-86-4 | 0.99 | 0.993 | GC | 0.0004 |
| 2-Ethoxyethanol | S.D.Fine Chem. Ltd | 110-80-5 | 0.98 | 0.987 | GC | 0.0004 |
| 2-Butoxyethanol | S.D.Fine Chem. Ltd. | 111-76-2 | 0.98 | 0.994 | GC | 0.0005 |

* GC = Gas chromatography.