Fluid Phase Equilibria 367 (2014) 7–21

Contents lists available at ScienceDirect

Fluid Phase Equilibria

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

Thermodynamics of binary mixtures: The effect of substituents in aromatics on their excess properties with benzylalcohol

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ARTICLE INFO

Article history:
Received 15 September 2013
Received in revised form 12 January 2014
Accepted 20 January 2014
Available online 30 January 2014

Keywords:
Density
Excess molar volume
Speed of sound
Redlich–Kister equation
Molecular interaction

ABSTRACT

Density (ρ) at 298.15–313.15 K and speed of sound (u) at 303.15 and 313.15 K have been measured for the binary mixtures of benzyl alcohol with chloro and nitro toluenes over the entire composition range. Experimental density and speed of sound data were used to compute excess molar volume (V^E), excess speed of sound (u^E), isentropic compressibility (κ_S) and excess isentropic compressibility (κ_S^E). Further, excess properties were fitted with Redlich–Kister and Hwang equations. Finally, speed of sound data was analyzed in terms of theoretical models, Schaaff's collision factor theory (CFT) and Jacobson's free length theory (FLT).

1. Introduction

For many years the chemical industry has recognized the importance of thermodynamic and physical properties of liquids and their mixtures are essential in design calculations involving chemical separations, fluid flow, and heat transfer. The study of molecular interaction in the liquid mixtures is of considerable in the elucidation of the structural properties of the molecules. The intermolecular interactions influence the structural arrangement along with the shape of the molecules. The sign and magnitude of these properties guide us to understand possible interactions between the component molecules [1–4]. The interaction between hydroxyl group of aromatic alcohol [5] and solvents with non-polar and polar solvents play a crucial role in the structural effects, molecular level and in practical applications. Further, the knowledge of structure and molecular interactions of liquid mixtures is very important from fundamental and engineering point of view. This information is very useful in design of industrial process and in the development of theories part of the liquid state and predictive methods. Since density and speed of sound fundamentally related to the binding forces that all exciting between the component molecules [6,7]. From a practical point of consideration, these properties are necessary for the development of thermodynamic models required in adequate and optimized processes of the chemical, petrochemical, pharmaceutical, and other industries. The experimental data on macroscopic properties such as excess molar volumes, excess viscosities, speed of sound and refractive index are often useful to understand the nature of homo and hetero molecular interactions, between component molecules. As the literature was scrutinized with respect to the factors effecting the thermodynamically properties of binary mixtures, it was seen that there are many systematic studies governing these factors [8–10]. In the present study, densities (ρ) of pure liquids and their mixtures from 298.15 to 313.15 K at the interval 5 K and speed of sound data at 303.15 and 313.15 K for five binary mixtures, namely benzylalcohol with o-chlorotoluene, m-chlorotoluene, p-chlorotoluene, o-nitrotoluene and m-nitrotoluene, were measured over the entire composition range. From measured density and speed of sound data, excess molar volumes (V^E), excess speed of sound (u^E) and excess isentropic compressibility (κ_S^E) were calculated. Further, the experimental speed of sound data was compared with theoretical models proposal by Schaaff's collision factor theory (CFT) and Jacobson's free length theory (FLT). The systems chosen in the present investigation were very interesting from practical point of view due to their various industrial and consumer applications. Benzylalcohol is a versatile compound used as a solvent for gelatin, cellulose acetate, shellac and for pharmaceutical aid as an antimicrobial agent [11,12], as cosmetic agent in perfumery, in microscopy as an embedding material, and in veterinary

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0378-3812/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.fluid.2014.01.019

applications [13]. Chlorotoluenes are used as intermediates in the pesticides, pharmaceutical, peroxides, dyes, dyestuffs, solvents and other industries [14]. Nitrotoluene is used in the synthesis of intermediates for azodyes, sulfur dyes, rubber chemicals and agriculture chemicals [15].

The present work was taken to understand the effect of o-chloro and o-nitro groups and their orientation in toluene which may influence both the sign and magnitude of excess properties when they mixed with benzyl alcohol.

2. Experimental

2.1. Materials

All the chemicals used in the present work were of analytical reagent grade procured from S.D. Fine Chemicals Ltd., India and Merck and their purities were as follows: benzyl alcohol 99.5%, o-chlorotoluene 99.5%, m-chlorotoluene 99.0%, p-chlorotoluene 99.0%, o-nitrotoluene 99.5% and m-nitrotoluene 99.5%. Prior to experimental measurements, all the liquids were purified as described in the literature [16,17] and given in Table 1 along with their CAS number and water content. Further, after fractional distillation, the purity of chemicals was checked by comparing the measured densities and speed of sound, which were in good agreement with literature values [18–22,32–36] as shown in Table 2.

2.2. Apparatus and procedure

All the binary liquid mixtures are prepared by weighing an appropriate amount of pure liquids an electronic balance (Afoset, ER – 120A, India) with a precision of ±0.1 mg by syringing each component into airtight stopper bottles to minimize evaporation losses. The uncertainty of the mole fraction was $\pm 1 \times 10^{-4}$. After mixing the sample, the bubble free homogenous sample was transferred into the U-tube of the densitometer through a syringe. The density measurements were performed with a Rudolph Research Analytical Digital Densitometer (DDM-2911 Model), equipped with a built-in solid-state thermostat and a resident program with accuracy of temperature of 303.15 ± 0.03 K. The uncertainty density measurement liquid mixtures are $\pm 2 \times 10^{-5}$ g cm^{-3}. Proper calibrations at each temperature were achieved with doubly distilled, deionized water and with air as standards. The ultrasonic speed in pure liquids and in their mixtures were measured by using a multi frequency (M-82 Model, Mittal Enterprise, New Delhi, India) single-crystal variable-path, operated at 2 MHz at 303.15 and 313.15 K by using a digital constant temperature water bath. The uncertainty in the measurement of speed of sound is ±0.3%. The temperature stability is maintained within ±0.05 K by circulating thermostatic water bath around the cell with a circulating pump. The present investigation has been devoted to the study of densities, speed of sounds of binary liquid mixtures at different temperatures and at a pressure of 0.1 MPa.

3. Results and discussion

3.1. Excess molar volume

The measured densities of liquid mixtures were given in Table 3 for studied binary mixtures of benzylalcohol with o-chlorotoluene, m-chlorotoluene, p-chlorotoluene, o-nitrotoluene and m-nitrotoluene at temperature range from 298.15 to 313.15 K. The excess molar volume (V^E) of all the binary mixtures were calculated from the measured densities using the following equation and these values are also given in Table 3 along with the graphical representation in Figs. 1–5. In order to understand the effect

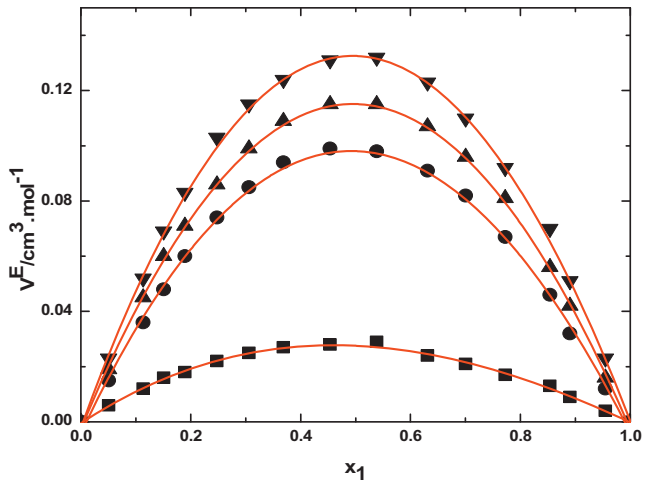

Fig. 1. Variation of excess volume (V^E) of the binary liquid mixture of benzylalcohol (1) with o-chlorotoluene (2) at 298.15 K (■), 303.15 K (●), 308.15 K (▲) and 313.15 K (▼).

of introduction of chloro and nitro group in toluene molecule that may influence both the sign and magnitude of V^E hence, binary V^E data of benzylalcohol with toluene [23] are also graphically represented along with those of chloro toluenes and nitro toluenes at 303.15 K in Fig. 6

$$V^E/\text{cm}^3\,\text{mol}^{-1} = [x_1M_1 + x_2M_2]/\rho_m - [x_1M_1/\rho_1 + x_2M_2/\rho_2] \quad (1)$$

where ρ_m the density of the mixture and, x_1, x_2, M_1, M_2, ρ_1, and ρ_2 are the mole fraction, molecular mass, and the density of pure component 1 and 2, respectively. The experimental excess volumes were also compared in terms of Redlich–Kister [24] and Hwang equation [25] which were included in Table 3.

The empirical relation proposed by Redlich–Kister is as follows:

$$V^E/\text{cm}^3\,\text{mol}^{-1} = x_1(1-x_1)[a_0 + a_1(2x_1-1) + a_2(2x_1-1)^2] \quad (2)$$

where a_0, a_1 and a_2 are the adjustable parameters and x_1 is the mole fraction of benzylalcohol. The values of these parameters were obtained by least-square method and fitted in Table 5.

$$\text{Hwang equation}: \quad V^E/\text{cm}^3\,\text{mol}^{-1} = x_1x_2[b_0 + b_1x_1^3 + b_2x_2^3] \quad (3)$$

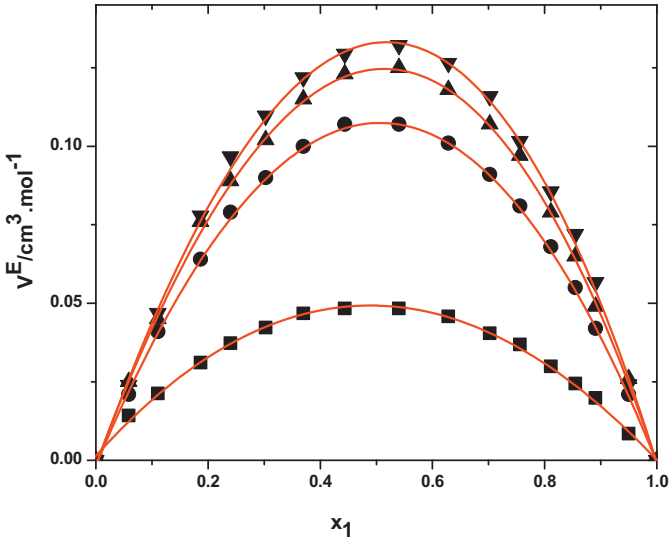

Fig. 2. Variation of excess volume (V^E) of the binary liquid mixture of benzylalcohol (1) with m-chlorotoluene (2) at 298.15 K (■), 303.15 K (●), 308.15 K (▲) and 313.15 K (▼).