Effect of chain length of alcohol on thermodynamic properties of their binary mixtures with benzylalcohol

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ABSTRACT

Densities (ρ) of pure liquids and their mixtures have been measured over the entire composition range for the binary mixtures of benzylalcohol with 1-heptanol, 1-octanol, 1-nonanol and 1-decanol at 298.15 K to 313.15 K and at atmospheric pressure by using Rudolph Research Analytical Digital Density Meter (DDM-2911 model). Further, the speed of sound (u) for the above said mixtures were also measured at 303.15 K and 313.15 K. The experimental density data were used to compute excess molar volumes (V^E) and compared with predictive expression proposed by Redlich–Kister equation. Excess speed of sound (u^E), isentropic compressibility (κ_S) and excess isentropic compressibilities (κ_S^E) were evaluated from experimental sound velocity and density data. Moreover, the experimental speed of sound data was compared in terms of theoretical models proposed by Schaaff's collision factor theory (CFT) and Jacobson's free length theory (FLT). The experimental results were discussed in terms of intermolecular interactions between component molecules.

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1. Introduction

Thermodynamic and physical properties of liquid mixtures are used in design calculations involving chemical separation, fluid flow, heat transfer and industrial applications. The variations in density, speed of sound and properties derived using them of binary mixtures of alcohols with a variety of organic liquids which differ in molecular size, shape, chain length and degree of molecular association of normal alcohols have been reported earlier [1–3]. The study of molecular interaction in the liquid mixtures containing one of the components as alcohol is of considerable in the elucidation of the structural properties of the liquid mixtures.

The speed of sound and consequently the isentropic compressibility can be regarded as thermodynamic properties, provided that a negligible amount of ultrasonic absorption of the acoustic waves of low frequency and of low amplitude is observed, in which case, the ultrasonic absorption of the acoustic waves is negligible [4,5]. Knowledge of speed of sound and isentropic compressibility of liquid mixtures is essential in many important applications involving chemical, industrial and biological processes [6]. In the present study, densities (ρ) of pure liquids and their mixtures

namely benzylalcohol with 1-heptanol, 1-octanol, 1-nonanol and 1-decanol were measured over the entire composition range at 298.15 K, 303.15 K, 308.15 K and 313.15 K and speed of sound data at 303.15 K and 313.15 K. From these data excess volumes (V^E) and excess isentropic compressibility (κ_S^E) were calculated. The liquid components selected as binary mixtures, are well known organic liquids and also had wide range of applications various fields of chemistry besides being used in industries and routine analytical work. Benzylalcohol is a versatile compound used as a solvent for gelatin, cellulose acetate, shellac and for pharmaceutical aid as an antimicrobial agent [7], in perfumery, in microscopy as an embedding material, and in veterinary applications [8]. Alcohols are interesting simple examples of biological and industrial important amphiphilic materials and also versatile solvents used in chemical and technological processes are inexpensive and easily available at high purity [9]. A survey of the literature has shown that thermodynamic properties of binary liquid mixtures containing benzylalcohol and aromatic hydrocarbons [10], and alcohols [11–13] and chloro alkanes were reported earlier [14]. To our best of knowledge, no systematic study on excess volumes (V^E) and excess isentropic compressibility (κ_S^E), for a series of higher alcohols with benzylalcohol, hence we report here new V^E and κ_S^E data for the binary mixtures of benzylalcohol with alcohols (C$_7$–C$_{10}$). In alcohols the —OH group consists one hydrogen bond donor i.e. H— atom and two acceptors it means two lone pair of electrons on the oxygen atom. It has been reported that the strength of association in alkanols decreases as the carbon chain length in the molecule

increases [15,16]. Further, the experimental sound velocity data were also compared with theoretical models proposed by Schaaff's collision factor theory (CFT) [17] and Jacobson's free length theory (FLT) [18,19]. The present work was under taken to know the effect of temperature and chain length of alcohols when mixed with benzylalcohol that may induce changes in sign and magnitude of excess thermodynamic functions.

2. Experimental

2.1. Materials

All the chemicals used in the present work were of analytical reagent grade procured from Merck and their purities were as follows: benzylalcohol 99.5%, 1-heptanol 99.5%, 1-octanol 99.5%, 1-nonanol 99.6% and 1-decanol 99.5%. Prior to experimental measurements, all the liquids were purified as described in the literature [20,21]. Further, 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 ppm to 100% by conductometric titration with dual platinum electrode and given in Table 1 along with their CAS number and purity. The purity of the sample was further confirmed by GLC single sharp peak. Before use, the chemicals were stored over 0.4 nm molecular sieves for about 72 h to remove water and were later degassed. Density (ρ), speed of sound (u) and isentropic compressibility (κ_S) for pure component liquids compared with the available literature values [10,13,22–27] and found in good agreement 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 Density Meter (DDM-2911 Model), equipped with a built-in solid-state thermostat and a resident program with accuracy of temperature of 303.15 K $\pm$ 0.03 K. The uncertainty in density measurement liquid mixtures are $\pm 2 \times 10^{-5}$ g cm^{-3} the details of measurement of density were reported earlier [28]. 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 ultrasonic interferometer (M-82 Model, Mittal Enterprise, New Delhi, India) single-crystal variable-path, operated at 2 MHz, at 303.15 K and 313.15 K by using a digital constant temperature water bath. The uncertainty in the measurement of ultrasonic sound velocity is $\pm 0.3\%$. The temperature stability is maintained within ± 0.01 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. In order to minimize the uncertainty of the measurement, several maxima are allowed to pass and their number (50) in the present study is counted. All maxima are recorded with the highest swing of the needle on the micrometer scale. The total distance d (cm) moved by the reflector is given by $d = n\lambda/2$, where λ is the wave length. The frequency, ν, of the crystal being accurately known (2.0 MHz), the speed of sound, u in m s^{-1} is calculated by using the relation $u = \nu\lambda$.

3. Equations

The experimental densities of mixtures were given in Table 3 for all the binary mixtures of benzylalcohol with 1-heptanol, 1-octanol, 1-nonanol and 1-decanol over the entire composition range at from 298.15 K to 313.15 K. The excess molar volume (V^E) of all the binary mixtures were calculated presented in Table 3, from the measured densities using the following equation

$$V^E \ (\text{cm}^3 \, \text{mol}^{-1}) = \left[\frac{x_1 M_1 + x_2 M_2}{\rho_m} \right] - \left[\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right] \tag{1}$$

where x_i is the mole fraction of component i ($i = 1, 2$) in the mixture; M_i is the molar mass ρ and ρ_i are the measured density of the mixture and the pure component i, respectively. The uncertainties in excess volume were of ± 0.005 cm^3 mol^{-1}.

The comparison of calculated V^E data (using Eq. (1)) and predicted V^E in terms of Redlich–Kister equation also shown in Table 3.

From the result of speed of sound (u), excess speed of sound (u^E), and isentropic compressibilities (κ_S) were calculated for binary system of benzylalcohol with 1-heptanol, 1-octanol, 1-nonanol and 1-decanol at 303.15 K and 313.15 K by using the following equations and it is given in Table 4 along with graphical representation in Figs. 5–8.

The excess speed of sound (u^E) and ideal density (ρ^{id}) of the binary mixtures under the investigation [29] were calculated from the following equations

$$u^E = u - u^{id} = u - (\rho^{id} \kappa_S^{id})^{-1/2} \tag{2}$$

$$\rho^{id} = \sum_i \phi_i \rho_i \tag{3}$$

$$\phi_i = \frac{x_i v_i}{\sum_i x_i v_i} \tag{4}$$

The corresponding excess isentropic compressibilities (κ_S^E) were obtained from the relation [30]

$$\kappa_S = u^{-2} \rho^{-1} \tag{5}$$

$$\kappa_S^E = \kappa_s - \kappa_S^{id} \tag{6}$$

where κ_S^{id} is the ideal value of the isentropic compressibility and was calculated from the following equation [30].

$$\kappa_s^{id} = \sum_{i=1}^{2} \phi_i \left[\kappa_{s,i} + TV_i \left(\frac{\alpha_i^2}{C_{p,i}} \right) \right] - \left\{ \frac{T \left(\sum_{i=1}^{2} x_i V_i \right) \left(\sum_{i=1}^{2} \phi_i \alpha_i \right)^2}{\sum_{i=1}^{2} x_i C_{p,i}} \right\} \tag{7}$$

here, $C_{p,i}$ and α_i are the molar heat capacity and the thermal expansion coefficient of the ith component respectively. The value of C_{pi} and α_i obtained and evaluated from literature [22,23] and presented in Table 2.

The experimental V^E values and κ_S^E data in have been fitted to Redlich–Kister type polynomial equation [31].

$$Y^E = x_1 x_2 \sum_{i=0}^{n} a_i (x_1 - x_2)^i \tag{8}$$

where $Y^E = V^E$, u^E or κ_S^E the subscription 'i' in the equation takes value from 0 to 2; a_i is the adjustable parameter of the function and are determined using the least-squares method. The corresponding standard deviations $\sigma(Y^E)$ have been computed using the relation

$$\sigma(Y^E) = \left[\sum \frac{(Y_{\text{exp}}^E - Y_{\text{cal}}^E)^2}{m - n} \right]^{1/2} \tag{9}$$

where 'm' is the total number of experimental points and 'n' is the number of coefficients in (Eq. (8)), and the standard deviations of all the binary mixtures have been presented in Table 5.