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Study on solution properties of some industrially important solvents with an aromatic alcohol

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ABSTRACT

Densities (ρ) of pure liquids and their mixtures have been measured at 298.15 K to 313.15 K and atmospheric pressure over the entire composition range for the binary mixtures of benzylalcohol, with 1,2-dichlorobenzene, 1,3-dichlorobenzene, and 1,2,4-trichlorobenzene by using Rudolph Research Analytical digital densitometer (DDH-2911 model). Further, the ultrasonic sound velocities for the above said mixtures were also measured at 303.15 K and 313.15 K. The measured density data were used to compute excess molar volumes (V^E) and these were compared with Hwang equation. Isentropic compressibility (κ_S) and excess isentropic compressibilities (κ_S^E) were evaluated from experimental sound velocity and density data. Moreover, the experimental sound velocities were analyzed in terms of theoretical models namely collision factor theory (CFT) and free length theory (FLT). The experimental results were discussed in terms of intermolecular interactions between component molecules.

1. Introduction

Mixing effects of large number of compounds and their mixtures which are used in the process industry are rather difficult to be known, hence the investigation of thermodynamic properties such as densities, ultrasonic sound velocities, enthalpies and entropies which give an idea of to what extent the deviations from non-ideality of organic mixtures at various temperatures is of great importance. Selection of systems for thermodynamic investigation should be based not only on the molecular structure of the industrial components but also on their industrial and ecological importance. A vast knowledge of thermodynamic properties binary liquid mixtures is essential in many industrial applications such as design calculation, heat transfer, mass transfer, fluid flow, etc. [1]. Further non-ideal thermodynamic behavior of liquid mixture may be discussed in terms of differences in molecular size and shape, dispersion forces, polarity, polarizability, molecular association, etc. The liquid components selected as binary mixtures, are well-known organic liquids and also had a wide range of applications at various fields of chemistry besides being used in industries and routine analytical work. In the present study an attempt has been made to know the nature of molecular interactions occurring between binary mixtures of of benzylalcohol with 1,2-dichlorobenzene,1,3-dichlorobenzene, and 1,2,4-trichlorobenzene by measuring densities (ρ), at 298.15 K to 313.15 K and speeds of sound (u) at 303.15 K and 313.15 K have been measured over the entire composition range. Benzylalcohol is an important solvent for gelatin, cellulose acetate, and shellac [2]. 1,2-dichlorobenzene is used as an intermediate for dyes, and certain agricultural chemicals. 1,3-dichlorobenzene is widely used in the manufacture of poly resin, used as a room deodorant blocks and moth control. 1, 2, 4-trichlorobenzene is used in the manufacture of the herbicide, in some pesticides, as a dye carrier in dielectric field, as an organic intermediate and a chemical manufacture solvent in lubricants [3]. From these density data, excess molar volumes (V^E) and excess isentropic compressibility (κ_S^E) were calculated. Further, the experimental sound velocity data were compared with theoretical models proposed by Schaaff's collision factor theory (CFT) [4] and Jacobson's free length theory (FLT) [5,6].

The present work was taken to know the effect of the introduction of a chloro group and their orientation in chlorobenzene molecule that may influence both the sign and magnitude of excess volume and excess isentropic compressibility.

2. Experimental

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%, 1,2-dichlorobenzene 99.5%, 1,3-dichlorobenzene 99.5%, and 1,2,4-trichlorobenzene 99.6%. Prior to experimental measurements, all the liquids were purified as described in the literature [7,8]. The purity samples were attained by fractional distillation and the purity of chemicals was checked by comparing the measured densities and ultrasonic sound velocities, which

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were in good agreement with literature values [9,10] and these are given in Table 1. 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.

3. Measurements

All the binary liquid mixtures are prepared by weighing an appropriate amount of pure liquids in 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 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 303.15 K ± 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. A multi frequency ultrasonic interferometer (M-82 Model, Mittal Enterprise, New Delhi, India) operated at 2 MHz, was used to measure the ultrasonic velocities of the binary liquid mixtures 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 ±0.3%. The temperature stability is 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 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 ms^{-1} is calculated by using the relation $u = \nu\lambda$.

Table 1
Densities (ρ) sound velocity (u), thermal coefficient (α) and heat capacity (C_p) for pure component liquids at temperatures from 298.15 to 313.15 K along with the literature values.

T/K	ρ (g cm^{-3})		u (m s^{-1})		α (kK^{-1})	C_p (J.mol^{-1}.k^{-1})
	Exp.	Lit.	Exp.	Lit.		
Benzylalcohol						
298.15	1.03851	1.03856	–	–	–	–
303.15	1.03760	1.03700 [9]	1514	1511 [9]	0.7402	224.35 [22]
308.15	1.02785	–	–	–	–	–
313.15	1.02691	–	1519	–	0.7456	227.62 [22]
1,2-dichlorobenzene						
298.15	1.30034	1.30090 [10]	–	–	–	–
303.15	1.29545	1.29540 [10]	1266	1265 [10]	0.8629	171.76 [10]
308.15	1.28913	1.28970 [10]	–	–	–	–
313.15	1.27653	–	1237	–	0.8768	173.86 [22]
1,3-dichlorobenzene						
298.15	1.28345	1.28280 [10]	–	–	–	–
303.15	1.27772	1.27779 [10]	1237	1238 [10]	0.8862	171.25 [10]
308.15	1.27219	1.27210 [10]	–	–	–	–
313.15	1.27210	–	1228	–	0.9685	173.24 [22]
1,2,4-trichlorobenzene						
298.15	1.44841	1.44841 [10]	–	–	–	–
303.15	1.44248	1.44243 [10]	1252	1256 [10]	0.8303	195.92 [10]
308.15	1.43645	1.43645 [10]	–	–	–	–
313.15	1.41951	–	1232	–	0.8426	197.26 [22]

References: 1 Ref: [9], 2 Ref: [10] and 3 Ref [22].

4. Results and discussion

The non-ideal binary mixture behavior, represented by in terms of excess molar volume (V^E), was computed from the experimentally determined density data using following equation

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

where, x_i is the mole fraction of component i(i = 1,2) in the mixture; M_i is the molar mass ρ and ρ_i are the measured density of the mixture and the pure component i, respectively. The computed V^E data was also given in Table 2 along with the predicted in terms of Hwang equation [11]. The methods and calculation of V^E in terms of Hwang equation were described earlier [12–15]. The V^E data for all the binary systems of benzylalcohol with 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene were graphically represented in Figs. 1–3. Further, the binary V^E data for benzylalcohol and chlorobenzene mixture [16] was also represented in Fig. 4 at 303.15 K to study the effect of addition of the second/third chloro group in chlorobenzene molecule on how does it is influencing the sign and magnitude of excess volume of binary mixtures that were under the present investigation. In general, the values of V^E can be considered as arising from the two types of interactions between the component molecules:

i) A physical interaction consisting dispersion forces or weak dipole–dipole interactions, making a positive contribution
ii) A chemical or specific interaction, which includes charge–transfer force, forming H-bonding and other complex-forming interactions, resulting in a negative contribution to V^E values.

Apart from these interactions, negative contribution may also be due to the different shapes and sizes of component molecules, which might allow them to fit into each other's structures, reducing volume and resulting in negative V^E values. However, liquids of nearly equal molecular size usually mix to give a positive contribution to V^E [17,18]. A perusal of V^E data in Table 2 shows that the factors that are responsible for positive contribution in all the binary mixtures of benzylalcohol with di/trichlorobenzenes. It is evident from the plots in Figs. 1–3 suggest that, V^E data is positive for the mixtures of benzylalcohol with isomeric chlorobenzenes and negative in the mixture containing benzylalcohol with chlorobenzene. The decrease in negative values of V^E with increase in number of chloro groups in chlorobenzene molecule reveals that dipole–dipole interactions are becoming weaker from 1,2-dichlorobenzene to 1,2,4-trichlorobenzene.

Algebraic values of excess volumes for the systems of benzylalcohol with chlorobenzenes fall in the order:

1,2-dichlorobenzene < 1,3-dichlorobenzene < 1,2,4-trichlorobenzene.

The difference in V^E values observed between dichloro and trichlorobenzenes is probably because of the difference in their shapes which leads to different alignments in the liquid mixture. Further, the chlorine atom at the 4th position in 1,2,4-trichlorobenzene offers the least steric hindrance to benzylalcohol molecules and thus the electron donor–acceptor interactions in it are lower than those of 1,2-dichlorobenzene and 1,3-dichlorobenzene. However, V^E values for mixtures of benzylalcohol with 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene are algebraically smaller than those for mixtures of benzylalcohol with chlorobenzene [16]. This shows that the addition of the second or third chloro group on chlorobenzene ring has influenced the sign and magnitude of excess volume to a significant extent. This observation is in line which were reported earlier for the binary mixtures of dimethylsulphoxide and dimethylformamide with di/trichlorobenzenes [19,20].

Furthermore, a comparison between experimental excess molar volume and the predicted in terms of Hwang equation shows that the computed excess molar volumes give good estimation in all the binary mixtures that are under the present investigation.