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Study on thermo physical properties of binary mixture containing aromatic alcohol with aromatic, substituted aromatic amines at different temperatures interms of FT-IR, ^{1}H NMR spectroscopic and DFT method

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ABSTRACT

The densities (ρ) of binary mixtures of benzyl alcohol (BA) with aniline (A), N-methylaniline (NMA), *N,N*-dimethylaniline (NNDMA), *o*-chloroaniline (*o*-CA) and *m*-chloroaniline (*m*-CA) have been analysis at different temperatures. Further, the speeds of sound (u) were measured at 303.15 K and 313.15 K temperatures of the above said systems. The excess molar volumes (V^E) and excess isentropic compressibilities (κ_S^E) calculated by using experimental data. The measured thermo physical properties were fitted in terms of R.K & HW equations. The measured u values were compared with Jacobson's free length theory (FLT) and Schaff's collision factor theory (CFT). The experimental and theoretical investigations have been playing a dominant role in the elucidation of hydrogen bond in solute, solvent and solute-solvent of the mixture. The results has been further confirmed by the existence of solvent-solute interactions of hydrogen bonding between benzyl alcohol and amines through Fourier transform Infrared and Nuclear Magnetic Resonance data at equimolar composition. The analysis of intermolecular hydrogen bond association through electron density, natural bond orbital analysis using density functional theory (DFT). The position and design of intensity of −OH and $-NH_2$ bands as per Nuclear Magnetic Resonance and Fourier transform Infrared spectroscopic data strongly supported by the conclusion that molecular association of inter molecular hydrogen bonding through excess properties have been observed. Further, the molecular dynamics (MD) simulations have been performed in liquid phase used to calculate the radial distribution functions of the pure components and mixtures with equimolar mole fractions at 298.15 K and 1 atm. From the molecular dynamics simulation and quantum calculations it has been confirmed the existence of H-bond between component molecules.

1. Introduction

Thermo physical properties of binary liquid mixtures, having molecules that measure ready for undergoing interactions, show vital deviation from ideality due to arising of structural changes. Systematic experimental study on thermo physical properties of binary mixtures is being an important tool/guide for the investigation of the molecular interactions. The derivation of various excess functions from the measured properties of individual pure and of mixture components and the analysis of the latter in terms of applications of several statistical theories of solutions give a better understanding of interactions present at molecular level. Moreover, the present experimental work on density (ρ) and speed of sound

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(u) of binary systems are important not only to sensible viewpoint, but also towards theoretical consideration. The investigation of the speed of sound is one of the valuable relatively simple and reliable tool for the study of liquids and liquid mixtures. Further, the chemical industries have identified the key role of the thermodynamic properties involving in design calculations for chemical separation, heat and mass transfer and fluid flow. When two or more component molecules are mixed with one another to form a liquid mixture, it causes a drastic effect on the properties of resulting solution and differences in the intermolecular interactions of component molecules.

The solvent-solute interactions between liquid molecules interms of excess thermodynamic functions produce a vital role within the development of molecular sciences and structural arrangement of the molecules [1,2]. Generally, present studying systems play a key role in different biological applications such as protein folding [3,4], membrane assembly [5], electrochemical cells [6] and heterogeneous catalysis [7]. The liquids that were selected within the investigation having a variety of commercial applications. Benzyl alcohol is utilized as versatile solvent in the synthesis of perfuming products and in veterinary medicines [8]. The utility of amines involves in pharmaceutical, agricultural, rubber chemicals. The industrial importance of chloroaniline is vast which include in oil solvents, fungicides and an intervening agent in the synthesis of azo dyes, agricultural chemicals and prescription drugs. Aniline is the starting material in the dye manufacturing industry. It forms aniline colors when combined with other substances, particularly chlorine or chlorates. Aniline is also important in the manufacture of rubber-processing chemicals, explosives, plastics, antioxidants and varnishes. Amines take part in many kinds of chemical reactions and offer many industrial applications. *o*-chloroaniline is used as an intermediate in the production of a number of products, including agricultural chemicals, azo dyes and pigments and pharmaceuticals. *o*-chloroaniline is also used in petroleum solvents and fungicides. dimethylaniline is a key precursor to commercially important triarylmethane dyes such as malachite green and crystal violet. Dimethylaniline serves as a promoter in the curing of polyester and vinyl ester resins. Dimethylaniline is also used as a precursor to other organic compounds. A study of the in vitro metabolism of *N,N*-dimethyl aniline using guinea pig and rabbit preparations and GLC techniques has confirmed *N*-demethylation and *N*-oxidation as metabolic pathways, and has also established ring hydroxylation as a metabolic route [9]. The study of excess thermodynamic properties like V^E and κ_S^E of binary mixtures of benzyl alcohol and amines interms of spectral data are much of great significance to know the molecular interactions in binary liquid components in order to experience and to analysis the applicability of various solution theories and mathematical models [10].

In this research work, new experimental data report on density (ρ) and speed of sound (u) for the binary mixtures of benzyl alcohol with aniline (A), N-methylaniline (NMA), *N,N*-dimethylaniline (NNDMA), *o*-chloroaniline (*o*-CA) and *m*-chloroaniline (*m*-CA). Moreover, the experimental data were further confirmed by elucidation of hydrogen bonding between benzyl alcohol molecule and amine. The −OH group of benzyl alcohol also can act as proton acceptor due to lone electron pairs on oxygen atom and anilines which contain $-NH_2$ group serves as a π-type donor.

The measured u data for the studying systems were contrast in terms of CFT [11] and FLT [12,13] to check capability of these theories. FT-IR and NMR spectroscopic analysis were additionally collected within the present investigation to understand the prevalence of H- bonding interaction between benzyl alcohol with aniline and substituted aniline components.

2. Experimental section

2.1. Materials

The chemicals employed in this work have been of analytical grade. The purities of all the experimental liquids were analyzed by Gas Chromatography and the water content of samples were measured by Analab (Micro Aqua Cal 100) Karl Fischer Titrator and these were mentioned in Table S1. Further, the purity of chemical compounds was tested by comparison of densities (ρ) and speed of sound (u) measured in this work for pure compounds with literature values [14–39] were reported in Table S2.

2.2. Measurements

The analysis of densities were carried out with a Rudolph Research Analytical digital densimeter (DDH-2911 Model) equipped with a built-in solid state thermostat and a resident program with a temperature stability of ±0.02 K. The densities were automatically measured at the specified four temperatures by transferring the homogeneous and bubble free sample into the U-tube of the densimeter by using the medical syringe. The calibration of densimeter was performed at each specified temperature with air, de-ionized and double distilled water as standards and the detailed analysis procedure were previously reported [1,40]. The estimated uncertainty in density and excess volume was found to be $\pm 6 \times 10^{-5}$ gm. cm^{-3} and $\pm 0.003\ cm^3\ mol^{-1}$ respectively.

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 = 303.15 K and T = 313.15 K by using a digital constant temperature water bath. 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 λ is the wave length. The frequency, v, of the crystal being accurately known (2.0 MHz), the speed of sound, u in ms^{-1} is calculated by using the relation $u = v\lambda$. The details of analysis procedure have been previously reported [15,41]. The estimated uncertainty in speed of sound and excess isentropic compressibility values has been found to be $\pm 0.5\ m\ s^{-1}$ and $\pm 0.03\ T\ Pa^{-1}$respectively.

The FT-IR spectra of all pure and binary liquid mixtures had analyzed by using ALPHA FT-IR Spectrometer (Bruker, Germany). The samples were prepared by mixing of benzyl alcohol with aromatic amines in the 1:1 ratios. A drop of homogeneous sample has been placed to record the spectra in the region $4000–600\ cm^{-1}$ with $4.0\ cm^{-1}$ resolution. The same samples were measured by using JEOL RESONANCE JNM-ECS 400 ^{1}H NMR spectroscope operational at 400 MHz. In this NMR analysis of all samples containing $CDCl_3$ as an external solvent. All the experimental samples have been performed at room temperature.

2.3. Computational details

Gaussian 09 program suite [42] was used to perform all the optimization and frequency calculations of the complexes. The optimization and frequency calculations were accomplished using Moller-Plesset second order perturbation theory with B3LYP/6-311++G (d, p) level basis set. Interaction energies for all the optimized geometries were adjusted for the *Basis Set Superposition Error (BSSE)* utilizing Boys and Bernardi's counterpoise method