



Volumetric, acoustic and spectroscopic properties of 3-chloroaniline with substituted ethanols at various temperatures



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ABSTRACT

Densities (ρ), speeds of sound (u) and viscosities (η) have been measured for the binary mixtures containing 3-chloroaniline with substituted ethanol such as 2-phenylethanol, 2-chloroethanol and 2-aminoethanol at $T = (303.15 \text{ to } 318.15) \text{ K}$. These experimental data have been used to calculate excess volume (V^E), excess isentropic compressibility (κ_s^E), deviation in viscosity ($\Delta\eta$) and excess Gibbs energy of activation of viscous flow (G^{*E}). The excess partial molar volumes, $\bar{V}_{m,1}^E$ and $\bar{V}_{m,2}^E$, excess partial molar volumes $\bar{V}_{m,1}^{oE}$ and $\bar{V}_{m,2}^{oE}$ at infinite dilution have also been calculated. The variations in these properties with composition for all the binary mixtures suggest that loss of dipolar association, difference in size and shape of the component molecules, dipole–dipole interaction and hydrogen bonding between 3-chloroaniline with 2-phenylethanol, 2-chloroethanol and 2-aminoethanol were observed. The excess parameters have been fitted to Redlich–Kister equation and the results were analyzed in terms of specific interactions present in the mixtures. Furthermore, the FTIR spectra have been recorded at $T = 298.15 \text{ K}$ and found to be useful for understanding the presence of hydrogen bonding between nitrogen atom of amino group of 3-chloroaniline and hydrogen atom of the –OH group of substituted ethanol molecules in the liquid mixtures. A good agreement is obtained between excess quantities and spectroscopic data.

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1. Introduction

Densities (ρ) speeds of sound (u) and viscosities (η) of solutions are very important properties especially for the chemical design and for the optimization of chemical processes. The study of these properties plays an important role in many industrially interesting systems such as organic synthesis, ion extraction systems, gas adsorption solvents and mass transfer phenomena. Furthermore, the study of excess thermodynamic and transfer properties for binary mixtures will provide a lot of important information concerning the deeper understanding of the molecular liquid structure and intermolecular interactions. This work is a part of our program to provide data for the characterization of the molecular interactions between solvents in binary systems [1–3]. The liquids were chosen for the present study on the basis of their industrial importance. 3-Chloroaniline is a polar solvent and self-associated through hydrogen bonding of its amine group. The amino group

in 3-chloroaniline is an electron donor and also plays an important role as proton-acceptor center. 3-Chloroaniline is used as an intermediate in the production of a number of products, including agricultural chemicals, azo dyes and pigments, bactericide or biocide and pharmaceuticals. On the other hand, 2-chloroethanol is a polar, bi-functional compound, consisting of both hydroxyl group as a proton donor and halogen atom as a proton acceptor. It is a versatile solvent used in many industrial areas and also a mutagenic chemical. Mono ethanolamine is a widely used agent in carbon dioxide and hydrogen sulfide removal processes. 2-Phenylethanol has found usage in artificial essences and as a base solvent for some flavor compounds.

In the present study, our focus is on the study of liquid mixtures of substituted ethanol with 3-chloroaniline because there have been few studies on these mixtures [4,5]. It is expected that there will be significant degree of H-bonding in these binary mixtures, because 3-chloroaniline and substituted ethanols both have a proton donor and a proton acceptor group [6]. To understand the possible associations between 3-chloroaniline and substituted ethanols through $\text{OH}\cdots\text{NH}_2$ and $\text{NH}_2\cdots\text{OH}$ bonds, we report the densities, speeds of sound and viscosities for three binary systems

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(3-chloroaniline with 2-aminoethanol, + 2-phenylethanol, + 2-chloroethanol) at $T = (303.15 \text{ K to } 318.15) \text{ K}$ and under 0.1 MPa pressure. The experimental data have been used to compute excess volume (V^E), excess isentropic compressibility (κ_s^E), deviation in viscosity ($\Delta\eta$) and excess Gibbs energy of activation of viscous flow (G^{*E}). The results are used to qualitatively discuss in terms of specific interactions between unlike molecules.

2. Experimental methods

2.1. Materials

All the chemicals (A.R. grade) were used in the present work supplied by Sigma–Aldrich, India and S.D. Fine Chem. Ltd., India. The mass fraction purities of all the chemicals are as follows: 3-chloroaniline (0.99), 2-phenylethanol (Sigma Aldrich) (>99%), 2-chloroethanol (>0.995) and 2-aminoethanol (>0.99). All the chemicals were further purified by the methods as described in the literature [7]. Prior to making experimental measurements, all the liquids were double distilled and partially degassed with a vacuum pump under an inert atmosphere. The mole fraction purities of the purified liquids as determined by gas chromatography are: 3-chloroaniline (0.995), 2-phenylethanol (0.995), 2-chloroethanol (0.995), and 2-aminoethanol (0.995). 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 are prepared by weighing an amount of pure liquids in an electric balance (ER-120A, Afoset, and India) with a precision of $\pm 0.1 \text{ mg}$ by syringing each component into air-tight stopper bottles to minimize evaporation losses. The uncertainty of the mole fraction is $\pm 1 \cdot 10^{-4}$. After mixing the sample, the bubble free homogenous sample is 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 is $\pm 0.03 \text{ K}$. The uncertainty of density measurement for liquid mixtures is $\pm 2 \cdot 10^{-3} \text{ g} \cdot \text{cm}^{-3}$ and the uncertainty of temperature $\pm 0.01 \text{ K}$. Proper calibrations at each temperature were achieved with doubly distilled, deionized water and with air as standards. The viscosities of pure liquids and their mixtures were determined at atmospheric pressure and at $T = (303.15 \text{ to } 318.15) \text{ K}$ by using an Ubbelohde viscometer, which was calibrated with benzene, carbon tetrachloride, acetonitrile, and doubly distilled water. The kinetic energy corrections were calculated from these values and they were found to be negligible. The Ubbelohde viscometer bulb has a capacity of 15 ml and the capillary tube has a length of about 90 mm with 0.5 mm internal

diameter. The viscometer was thoroughly cleaned and perfectly dried, filled with the sample liquid by fitting the viscometer to about 30° from the vertical and its limbs are closed with Teflon caps to avoid the evaporation. The viscometer was kept in a transparent walled bath with a thermal stability of $T = \pm 0.01 \text{ K}$ for about 20 min to obtain thermal equilibrium. An electronic digital stopwatch with an uncertainty of $\pm 0.01 \text{ s}$ was used for flow time measurements. The experimental uncertainty of viscosity estimated as $\pm 0.5 \text{ mPa} \cdot \text{s}$ and the uncertainty of temperature $\pm 0.1 \text{ K}$. 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 $T = (303.15 \text{ K to } 318.15) \text{ K}$ by using a digital constant temperature water bath. The uncertainty in the measurement of speed of sound is $\pm 0.3\%$ and the uncertainty of temperature $\pm 0.1 \text{ K}$. The working of the interferometer is tested by making measurements for pure samples of benzene, toluene, chloroform, chlorobenzene and acetone and the measured speeds of sound of these liquids is in good agreement with those reported in the literature [8]. The purity of all these solvents are compared with the measured density, speed of sound and viscosity of the pure liquids with the literature [7–25] and these are shown in table 2.

3. Results and discussion

The experimental values of density (ρ), viscosity (η) and speed of sound (u) of the binary liquid mixtures of 3-chloroaniline with substituted ethanols at $T = (303.15 \text{ to } 318.15) \text{ K}$ are presented in table 3.

Excess volumes (V^E) were calculated from the experimental density values, using the following equation:

$$V^E = \sum_{i=1}^2 x_i M_i (\rho^{-1} - \rho_i^{-1}), \quad (1)$$

where x_i , M_i and ρ_i are mole fraction, molar mass and density of pure components, respectively, ρ is the density of the mixture, the subscripts i and m represent pure components and mixture respectively. The excess volumes data are given in table 4 and graphically presented in figure 1. The excess volume has negative value for all studied systems over the whole composition range and at all experimental temperatures. The sign and magnitude of V^E varies with the physico-chemical and structural characteristics of the components of the liquid mixture on mixing. It is possible to identify favorable interactions, such as hydrogen bonds between hydrogen atom of hydroxyl ($-\text{OH}$) group of substituted ethanol and the nitrogen atom of amino group of 3-chloroaniline, leading to a contraction in volume, which results in negative V^E values. The hydrogen bonds between hydroxyl groups and amino group of 3-chloroaniline are stronger than those formed between homo-cooperative hydroxyl molecules [26]. The existence of strong $\text{O}-\text{H} \cdots \text{N}$ bond was also confirmed through NMR, IR and UV studies [27]. The same trend was observed with the system (water + ethanolamine) [28]. The differences in molar volume and free volume between the components of the mixtures should give a negative contribution to V^E .

TABLE 1

List of chemicals with CAS number, source, water content, analysis method and purity in mass fraction in this work.

Chemical name	CAS number	Source	Water content in mass fraction	Purification method	^a Analysis method	Purity in mass fraction (Final)
3-Chloroaniline	108-42-9	S.D. fine Chemicals, India	0.0004	Fractional distillation	GC	0.995
2-Phenylethanol	60-12-8	Sigma Aldrich India	0.0004	No further purification	GC	0.995
2-Chloroethanol	107-07-3	S.D. Fine Chemicals, India	0.0004	Fractional distillation	GC	0.995
2-Aminoethanol	141-43-5	S.D. Fine Chemicals, India	0.0004	Fractional distillation	GC	0.995

^a Gas chromatography.

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