



Study of intermolecular interactions in binary mixtures of 3-chloroaniline with isomeric chlorotoluenes at various temperatures



P. VenkateswaraRao^{a,*}, M. Chandra Shekar^b, L. Venkatramana^c, M. Gowrisankar^{d,**}, K. Ravindhranath^e

^a Department of Chemistry, R.V.R. & J.C.C. E. Acharya Nagarjuna University, Guntur, 522019, AP, India

^b Department of Physics, Vignana Institute of Technology and Science, Deshmukhi, 508284, Telangana, India

^c Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

^d Department of Chemistry, J.K.C.C. Acharya Nagarjuna University, Guntur, 522510, AP, India

^e Department of Chemistry, K L University, Guntur, 522502, AP, India

ARTICLE INFO

Article history:

Received 8 November 2015

Received in revised form 19 January 2016

Accepted 20 January 2016

Available online xxxx

Keywords:

Isomeric chlorotoluene
Charge-transfer complex
Partial molar volume
PFP theory

ABSTRACT

The densities (ρ), ultrasonic speeds (u), and viscosities (η) are reported for binary mixtures of 3-chloroaniline with isomeric chlorotoluenes such as *o*-chlorotoluene (*o*-CT), *m*-chlorotoluene (*m*-CT), and *p*-chlorotoluene (*p*-CT) over the entire range of mole fractions at 303.15, 308.15, 313.15 and 318.15 K and atmospheric pressure. The excess properties such as excess molar volume, excess isentropic compressibility and deviation in viscosity are calculated from the density, speed of sound and viscosity. Excess properties are correlated by the Redlich–Kister equation. The partial molar volumes, $\bar{V}_{m,1}$ and $\bar{V}_{m,2}$, partial molar isentropic compressibilities, $\bar{K}_{s,m,1}$ and $\bar{K}_{s,m,2}$, excess partial molar volumes, $\bar{V}_{m,1}^E$ and $\bar{V}_{m,2}^E$ and excess partial molar isentropic compressibilities, $\bar{K}_{s,m,1}^E$ and $\bar{K}_{s,m,2}^E$ over whole compositions range and at infinite dilutions have been calculated; partial molar volumes, $\bar{V}_{m,1}^{\circ}$ and $\bar{V}_{m,2}^{\circ}$, partial molar isentropic compressibilities, $\bar{K}_{s,m,1}^{\circ}$ and $\bar{K}_{s,m,2}^{\circ}$, excess partial molar volumes, $\bar{V}_{m,1}^{\circ E}$ and $\bar{V}_{m,2}^{\circ E}$, excess partial molar isentropic compressibilities, $\bar{K}_{s,m,1}^{\circ E}$ and $\bar{K}_{s,m,2}^{\circ E}$ of the components at infinite dilution have been calculated. The V^E results have been analyzed in the light Prigogine–Flory–Patterson theory. Analysis of each of the three contributions viz. interactional, free volume and P^* to V^E shows that interactional contribution is positive for all systems except *p*-chlorotoluene, which has small negative interactional contribution. The free volume effect and P^* contribution are negative for all the mixtures. The variations of these parameters with composition and temperature have been discussed in terms of intermolecular interactions prevailing in these mixtures.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Thermodynamic properties of mixtures that contain blends of organic solvents with isomeric chlorotoluenes are important from the technological and theoretical points of view, especially in probing molecular interactions between the different ingredients of the blends. It is well known that the study of excess thermodynamic properties like excess volume, excess isentropic compressibility is much important to understand the molecular interactions in liquid mixtures and develop and test the solution theories and mathematical models.

Studies of excess thermodynamic functions afford a means of ascertaining the molecular interactions and various other dynamic

processes that occur in solutions. The possible interactions that are frequently found in liquids or in blends of liquids are due to hydrogen bonding, loose complexation or charge transfer. The charge transfer complexes are of particular interest as they have diverse applications in chemistry (organic semiconductors) [1], physics and in biology [2], besides assisting in cellular metabolism in living systems. Further, the applications of spectrophotometric methods provide additional supporting evidence to the resulting conclusions obtained from these studies.

The liquids chosen in this study namely, 3-chloroaniline and *o*-/*m*-/*p*-chlorotoluene have industrial importance. 3-Chloroaniline is a polar solvent and self-associated through hydrogen bonding its amine group. The amino group in 3-chloroaniline is an electron donor and also play the role of 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. Chlorotoluenes are used as intermediates in manufacturing pesticide, pharmaceutical formulations and dye industries. A fundamental understanding of the mixture behavior of 3-

* Correspondence to: P. Venkateswara Rao, Department of Chemistry, R.V.R. & J.C.C.E. Acharya Nagarjuna University, Guntur, 522019, AP, India.

** Correspondence to: M. Gowri sankar, Department of Chemistry, J.K.C.C. Acharya Nagarjuna University, Guntur, 522006, AP, India.

E-mail addresses: pvr0.007.1@gmail.com (P. VenkateswaraRao), gowrisankar965@gmail.com (M. Gowrisankar).

chloroaniline with chlorotoluenes is therefore important from the technical and engineering standpoint.

Several researchers investigated density, speed of sound, and viscosity of binary mixtures of dimethylformamide with chlorotoluenes [3], tetrahydrofuran with chlorotoluenes [4], dimethylsulfoxide with chlorotoluenes [5] and benzyl alcohol with chlorotoluenes [6]. However, literature survey reveals that no study on excess thermodynamic properties for the systems containing 3-chloroaniline with isomeric chlorotoluenes was reported. The present work was taken to understand the effect of chloro group and its orientation in toluene molecules which may influence both the sign and magnitude of excess properties when mixed with 3-chloroaniline.

The present investigation is a continuation of our earlier research [7–10] on thermodynamic properties of binary liquid mixtures. In this paper we report measurements of densities, speeds of sound and viscosities for three binary systems, 3-chloroaniline + *o*-chlorotoluene, 3-chloroaniline + *m*-chlorotoluene and 3-chloroaniline + *p*-chlorotoluene at $T = (303.15\text{--}318.15)$ K and atmospheric pressure. From the experimental data, various physicochemical parameters, viz., V_m^E , κ_s^E , $\Delta\eta$ and G^{*E} of the mixtures; $\bar{V}_{m,1}$ and $\bar{V}_{m,2}$, $\bar{K}_{s,m,1}$ and $\bar{K}_{s,m,2}$, $\bar{V}_{m,1}^E$ and $\bar{V}_{m,2}^E$ and $\bar{K}_{s,m,1}^E$ and $\bar{K}_{s,m,2}^E$ over whole composition range; $\bar{V}_{m,1}^\circ$ and $\bar{V}_{m,2}^\circ$; $\bar{K}_{s,m,1}^\circ$ and $\bar{K}_{s,m,2}^\circ$; $\bar{V}_{m,1}^{\circ E}$ and $\bar{V}_{m,2}^{\circ E}$ and $\bar{K}_{s,m,1}^{\circ E}$ and $\bar{K}_{s,m,2}^{\circ E}$ of the components in the mixture at infinite dilution, have been calculated. The variations of these properties with composition of the binary mixtures are discussed in terms of molecular interactions between components and structural effects.

2. Experimental

2.1. Materials

All the chemicals (A.R. grade) were used in the present work supplied by S.D. Fine Chem. Ltd., India. The purities of all the chemicals as follows: 3-chloroaniline (>99%), *o*-chlorotoluene (99.5%), *m*-Chlorotoluene (99.0%) and *p*-chlorotoluene (99.0%). All the chemicals were purified by the methods as described in the literature [11,12]. Before measuring the pure samples, 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), *o*-chlorotoluene (0.995), *m*-chlorotoluene (0.995), and *p*-chlorotoluene (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. The purity of all these solvents are compared with the measured density, speed of sound and viscosity of the pure liquids with the literature [13–18] and these are shown in Table 2.

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 ± 0.1 mg by syringing each component into air-tight stopper bottles to minimize evaporation losses. The uncertainty of the mole fraction is $\pm 1 \times 10^{-4}$. After mixing the sample, the bubble free homogeneous 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 was ± 0.03 K. The uncertainty of density is $\pm 2 \times 10^{-3} \text{ g} \cdot \text{cm}^3$ and the uncertainty of temperature was ± 0.01 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 $T = 303.15$ to 318.15 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 had a capacity of 15 ml and the capillary tube had 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 were closed with Teflon caps to avoid the evaporation. The viscometer was kept in a transparent walled bath with a thermal stability of ± 0.01 K for about 20 min to obtain thermal equilibrium. An electronic digital stopwatch with an uncertainty of ± 0.01 s was used for flow time measurements. The experimental uncertainty of viscosity was estimated as $\pm 0.05 \text{ mPa} \cdot \text{s}$ and the uncertainty of temperature ± 0.1 K. A multi frequency ultrasonic interferometer (M-82 Model, Mittal Enterprise, New Delhi, India) operated at 2 MHz, was 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 was $\pm 0.3\%$ and the uncertainty of temperature was ± 0.1 K. The working of the interferometer was tested by making measurements for pure samples of benzene, toluene, chloroform, acetone and the measured speeds of sound of these liquids was in good agreement with those reported in the literature [19]. The experimental uncertainty of viscosity was estimated as $\pm 0.5 \text{ mPa} \cdot \text{s}$ and the uncertainty of temperature was ± 0.1 K, the viscosities of pure liquids and their mixtures were measured by using an Ubbelohde viscometer as described in the literature [18].

3. Results and discussion

The experimental values of density (ρ), viscosity (η) and speed of sound (u) of the binary mixtures of 3-chloroaniline with isomeric chlorotoluenes over the entire composition range, expressed in mole fraction of 3-chloroaniline at different temperatures are presented in Table 3.

The excess molar volume (V_m^E), deviations in isentropic compressibility (κ_s^E) and excess molar isentropic compressibility, $K_{s,m}^E$ have been calculated using the following equation [20,21]

$$V_m^E = V_m - (x_1 V_{m,1} + x_2 V_{m,2}) \quad (1)$$

$$\kappa_s^E = \kappa_s - \kappa_s^{\text{id}} \quad (2)$$

$$K_{s,m}^E = K_{s,m} - K_{s,m}^{\text{id}} \quad (3)$$

where V_m is the molar volume, subscripts 1 and 2 refer to 3-chloroaniline and isomeric chlorotoluenes, respectively; κ_s is the

Table 1
Provenance and purity of the materials used in this work.

Chemical name	CAS Number	Supplier	Water content in mass fraction	Analysis method ^a	Purity in mass fraction(after purification)
3-Chloroaniline	108-42-9	S.D. fine Chemicals, India	0.0004	GC	0.995
<i>p</i> -Chlorotoluene	106-43-4	Merck	0.0004	GC	0.995
<i>m</i> -Chlorotoluene	108-41-8	Merck	0.0004	GC	0.995
<i>o</i> -Chlorotoluene	95-49-8	Merck	0.0004	GC	0.995

^a Gas chromatography.

Download English Version:

<https://daneshyari.com/en/article/5410120>

Download Persian Version:

<https://daneshyari.com/article/5410120>

[Daneshyari.com](https://daneshyari.com)