Journal of Molecular Liquids 202 (2015) 158–164

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Thermodynamic properties of binary mixtures of aniline with halogenated aromatic hydrocarbons: Measurements and correlations

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ARTICLE INFO

Article history:
Received 8 November 2014
Received in revised form 15 December 2014
Accepted 16 December 2014
Available online 18 December 2014

Keywords:
Density
Speed of sound
Excess thermodynamic property
Collision factor theory
Free length theory
Molecular interaction

ABSTRACT

Density (ρ) and speed of sound (u) data have been measured at temperatures 303.15 and 313.15 K and at atmospheric pressure for five binary mixtures of aniline with chlorobenzene, bromobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene over the entire composition range. Experimental density and speed of sound data have been used to calculate the excess volumes (V^E), isentropic compressibilities (κ_s) and excess isentropic compressibilities (κ_s^E) of studied mixtures. The calculated V^E data were correlated with Redlich–Kister and Hwang polynomial equations. The experimental speed of sound data were analyzed in terms of Schaaff's collision factor theory (CFT) and Jacobson's free length theory (FLT). Results, obtained by measurements as well as calculations, were discussed in terms of intermolecular interactions between component molecules.

1. Introduction

Binary and multi component liquid mixtures are of great practical importance in many industrial processes. The study of thermodynamic properties of liquid mixtures is essential for the better understanding of non-ideal behavior of complex systems due to physical and chemical effects, which are caused by molecular interactions of unlike molecules [1,2]. The knowledge of the structure and molecular interactions of liquid mixtures is very important from fundamental and engineering point of view. Further, these properties are necessary for the development of thermodynamic models, required in adequate and optimized processes of the chemical, petro chemical, pharmaceutical and other industries. In addition, extensive information about structural phenomena of mixtures is of vital importance in the development of theories of the liquid state and predictive methods [3,4].

Thermodynamic investigation of liquid mixtures consisting of polar and non-polar components is of considerable importance in understanding the intermolecular interactions between component molecules and required for applications in several industrial and technological processes [5–7]. In continuation of our study on acoustic and volumetric properties of non-electrolyte liquid mixtures [8–10], in the present investigation, density (ρ) and speed of sound (u) were measured for five binary mixtures of aniline with chlorobenzene, bromobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene at temperatures 303.15 and 313.15 K and at atmospheric pressure. The liquids considered in the present study have many applications in various industries. The most important application of aniline is for the preparation of methylene biphenyl diisocyanate (MDI), besides its use in rubber processing, agriculture chemicals, herbicides, dyes and pigments and in the manufacture of drugs [11,12]. The major use of chlorobenzene is an intermediate in the production of commodities such as herbicides, dye stuffs and rubber while bromobenzene can be used to prepare the corresponding Grignard reagent and it is an ingredient in the manufacture of phenylcyclidine. 1,2-Dichlorobenzene is used as an intermediate for dyes and certain agricultural chemicals, whereas 1,3-dichlorobenzene is the largest and giving outlet is in the manufacture of polyresin and used as a room deodorant blocks and moth control. 1,2,4-Trichlorobenzene is used in the manufacture of herbicides, in some pesticides, as a dye carrier in dielectric field, as an organic intermediate and a chemical manufacture solvent in lubricants [13,14].

A survey of the literature has shown that thermodynamic properties for few binary mixtures containing aniline were reported [15–18]. As the literature was scrutinized with respective to the factors affecting the thermophysical properties, no experimental data have been so far reported on binary mixtures considered in this work. Experimental density data of studied binary mixtures have been used to calculate the excess volumes (V^E) and the calculated V^E data were correlated in terms of Redlich–Kister [19] and Hwang equation [20]. Moreover, the speed of

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http://dx.doi.org/10.1016/j.molliq.2014.12.024
0167-7322/

sound data of liquid mixtures were compared in terms of free length theory (FLT) [21,22] and collision factor theory (CFT) [23].

The present investigation was carried out to know the effect of the addition of chloro and bromo group in benzene molecule and addition of second and third chloro groups in benzene molecule that may influence both the sign and magnitude of excess volume and excess isentropic compressibilities when these components are mixed with aniline.

2. Experimental methods

2.1. Materials

All the liquids used in the present investigation were of Analytical grade (procured from S.D. fine Chemicals Ltd., India and Merck) and were as follows. Aniline (99.5%), chlorobenzene (99%), bromobenzene (99%), 1,2-dichlorobenzene (99.5%), 1,3-dichlorobenzene (99.5%), 1,2,4-trichlorobenzene (99.5%). Prior to making the experimental measurements, all the liquids were partially degassed with a vacuum pump under an inert atmosphere. Density and speed of sound data of pure substances and their comparison with literature values [15,17,24–28] were listed in Table 1.

2.2. Apparatus and procedure

All the binary liquid mixtures were prepared by weighing appropriate amounts of pure liquids using an electronic balance (Afcoset, 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 $\pm 1 \times 10^{-4}$. Densities of the pure liquids and their mixtures were measured by using Rudolph Research Analytical Digital Densimeter (DDM-2911 model) and these measurements were carried by carefully filling the sample in the U tube of the instrument with the help of a syringe. We have also ensured that no bubble formation during the measurement since cell should be air-free. The density was measured automatically at the specified temperature with an accuracy of ±0.00005 g.cm^{-3}. The instrument was calibrated once a day with double-distilled, deionized water and air as standards. The uncertainty in the density measurement is $\pm 2 \times 10^{-5}$ g·cm^{-3}. Speeds of sound measurements were performed using a commercially available single crystal ultrasonic interferometer (model F-05) from Mittal Enterprises, New Delhi, India, at 2 MHz frequency at various temperatures. A thermostatically controlled, well-stirred circulated water bath with a temperature controlled to ±0.01 K was used for all the speed of sound measurements. The uncertainty in a measured speed of sound is ±0.5 m·s^{-1}.

Table 1
Density (ρ) and speed of sound (u) of pure components at 303.15 K.

Component	ρ/g cm^{-3}		u/m s^{-1}	
	Present work	Literature	Present work	Literature
Aniline	1.01318	1.01317[b]	1614	1615[a]
Chlorobenzene	1.09582	1.09550[d]	1245	1248[c]
Bromobenzene	1.48142	1.48150[d]	1146	1244[c]
1,2-Dichlorobenzene	1.29924	1.29922[e]	1265	1261[f]
1,3-Dichlorobenzene	1.27715	1.27718[f]	1238	1242[f]
1,2,4-Trichlorobenzene	1.44215	1.44212[f]	1256	1260[f]

[a] [15].
[b] [17].
[c] [24].
[d] [25].
[e] [26].
[f] [27].

3. Results and discussion

The densities (ρ) of the mixtures, excess volumes (V^E) and correlated excess volumes in terms of Redlich–Kister [19] and Hwang [20] equations for all the binary systems of aniline with chlorobenzene, bromobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene at 303.15 and 313.15 K were given in Table 2. The calculations of excess volume (V^E) data, from densities of pure liquids and their mixtures were described [9] as

$$V^E/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1} = [x_1 M_1 + x_2 M_2]/\rho_m - [x_1 M_1/\rho_1 + x_2 M_2/\rho_2] \quad (1)$$

where x_1 and x_2 are the mole fractions of components 1 and 2, M_1 and M_2 are the molecular weight of components 1 and 2 and ρ_m, ρ_1 and ρ_2 are the density of mixture, component 1 and component 2, respectively.

The V^E data were graphically represented in Figs. 1 and 2 for all the binary mixtures over the entire composition range at T = 303.15 K and 313.15 K. An examination of V^E data in the above figures suggest that the property is negative for aniline with chloro/bromobenzene systems and positive deviation was observed for the systems containing 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene. The sign of excess volume (V^E) of a system depends on the relative magnitude of expansion and contraction of mixing of two liquids [14]. If the expansion factors dominate the contraction factors, then V^E becomes positive. On the other hand, if the contractive factors outweigh the expansive factors, then V^E become negative. The factors that are responsible for expansion in volume are as follows: i) loss of dipolar association (i.e. rupturing of H-bonding of component by the other or breaking up of associates held by weaker forces, namely, dipole–dipole or dipole–induced dipole interactions or by van der Waals forces), ii) the geometry of molecular structure, which does not allow fitting of the one component in to the others, and iii) steric hindrance, which opposes proximity of the constituent molecules. While the negative V^E values arise due to dominance of the following factors:

i. chemical interactions between constituent molecules such as hetero molecular associations through the formation of hydrogen bond known as strong specific interaction
ii. accommodation of molecules of one component into the interstitials of the molecules of the other component
iii. geometry of the molecular structure that favors fitting of the component molecules with each other.

An examination of curves in Figs. 1 and 2 indicate that the factors which are responsible for contraction in volume are dominant over the entire composition range for the binary mixtures of aniline with chlorobenzene and bromobenzene. On the other hand, expansion in volume factors is prevailing in the mixtures containing 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene mixtures. The algebraic excess volume data of all the binary mixtures will fall in the order:

chlorobenzene > bromobenzene > 1, 2-dichlorobenzene > 1, 3-dichlorobenzene > 1, 2, 4-trichlorobenzene.

The above order indicates that the extent of sign and magnitude of excess volume decreases by the introduction of second or third chloro groups in chlorobenzene molecule or replacement of a chloro group by a bromo group. Further, the more negative excess volume data of the mixture aniline with chlorobenzene when compared to bromobenzene may be explained as follows: Chlorobenzene is more reactive because the chlorine atom is bonded with sp^3 hybridized carbon atom and thereby it can be removed easily. Hence, the rate of reaction of chlorobenzene becomes faster and when compared to bromobenzene it is less reactive because of its double bond character between carbon and bromine atom. The less negative excess volume data of bromobenzene