Molecular interaction studies in binary mixtures containing aniline, toluene and n-butanol

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Abstract

Ultrasonic velocity and density values have been measured at 303 K in binary mixtures containing aniline, toluene and n-butanol; and the thermodynamical approach is applied to evaluate the mixtures' molar volume, adiabatic compressibility, intermolecular free length and excess values. The observed results are interpreted in terms of molecular interaction between the components of the mixtures. Observed excess values and their fittings of R-K type equations lend further support to the observation made in the binary system.

Key Words: Binary, velocity, density, molecular interactions, R-K type equations

1. Introduction

Velocity of sound waves in a medium is fundamentally related to the binding forces between the atoms or the molecules. Variation of ultrasonic velocity and related parameters throw much light upon the structural changes associated with the liquid mixtures having weakly interacting components [1–3] as well as strongly interacting components [4–6]. As such, ultrasonic techniques are very popular nowadays in examining the molecular interaction between the components. Understanding of intermolecular interactions between polar and non-polar component molecules finds applications in several industrial and technological processes [7, 8].

Ultrasonic and sonochemical reaction studies have been carried out by measuring ultrasonic velocities in the mixing of phenols (such as cresol) with esters (such as ethyl acetate and isoamyl acetate) as solvents by Renga Nayakulu et al. [9]. They found that the reaction rate decreases due to the passage of sonic waves through the medium. Such studies as a function of concentration are useful in gaining an insight into the structure and bonding of associated molecular complexes and other molecular processes. Further, they play an important role in many chemical reactions due to their ability to undergo self-association with manifold internal structures [3, 10].

Alcohols, in particular n-butanol, is found to predominantly exists as an azeotropic component in petrochemical industrial processes. The high boiling point (390.7 K) and the lower molecular radius (2.0896 nm) of n-butanol over its isomers is supposed to play a vital role in azeotropic formation with other organic liquids and this forms the central interest in choosing n-butanol mixtures in the present analysis. Aniline and toluene are popular industrial organic solvents and hence their interaction with the neighboring components needs to be revealed to understand the significance of their compositional behaviors. Further, mixtures with aniline/toluene as one component are indispensable for the industrial rectification column to avoid the formation of azeotropes. The wide survey of literature shows that there is no systematic study in the binary mixtures containing n-butanol, aniline and toluene. The intermolecular interaction existing between the components of these binaries need to be revealed to understand any physico - chemical process in these mixtures. Thus the present work aims at analyzing the intermolecular interactions of aniline and/or toluene with n-butanol. Ultrasonic techniques have been employed for the evaluation of molecular interaction in the chosen binary mixtures and it deals with the measurement of ultrasonic velocity and density at 303 K and computation of related parameters.

2. Experimental details

The mixtures of various concentrations in mole fraction by weight were prepared by taking purified AR grade samples at 303 K. The purification was done as per the standard procedures [11] and the purity was checked by comparing the density with those reported in the literature [12] and found to be closer. The ultrasonic velocities in liquid mixtures have been measured using an Mittal type ultrasonic interferometer working at 2 MHz frequency with an accuracy of $\pm$ 0.1 ms^{-1}. The density values are measured using a double capillary pycknometer with an accuracy of 3 parts in 10^5 for density. Each observation is repeated five times and the average is taken as final. Using the measured data, the acoustical parameters such as molar volume V, adiabatic compressibility β, inter molecular free length L_f, and their excess parameters have been calculated using the following standard thermodynamical expressions [13–16]:

$$V = \frac{M_{eff}}{\rho_{mix}} \tag{1}$$

$$\beta = \beta_{T\ id} - T\frac{\alpha_{id}^2 V_{id}}{Cp_{id}} \tag{2}$$

$$L_f = K_T \beta^{1/2} \tag{3}$$

$$A^E = A_{\exp} - A_{id} \tag{4}$$

and

$$A_{id} = \sum x_i A_i. \tag{5}$$

In these equations, $\beta_{T\ id}$ is the ideal isothermal compressibility and α_{id} is the ideal thermal expansion coefficient which are non-Gibbsian parameters and hence are volume fraction additive whereas the ideal molar volume V_{id} and the ideal specific heat capacity at constant pressure C_p are Gibbsian parameters and hence mole fraction additive. The calculated molar volume values are used to change the mole fraction to corresponding volume fraction of the components. Further, T is the absolute temperature, K_T is the temperature dependent constant having a value 201.1209×10^{-8} in M.K.S. system, $M_{eff} = \sum x_i m_i$ where, x_i is the mole fraction and m_i is

the molecular weight of ith component and A^E denotes the excess property of any given parameter, $A_{\exp}$ is the experimental value and A_{id} is the respective ideal value. All the standard values of the component liquids required to calculate the ideal values of the mixtures are taken from the literature [12, 17–19] and are listed in Table 1.

Table 1. Standard values of dipole moment D, density ρ, ultrasonic velocity U, isothermal compressibility β_T, thermal expansibility α and specific heat capacity C_p at constant pressure of the experimental liquids at 303 K.

Liquid	D	ρ (kgm^{-3})	U (ms^{-1})	β_T ($\times 10^{12}$ Pa^{-1})	α ($\times 10^3$ K^{-1})	C_p (kJkg^{-1}K^{-1})
Aniline	1.13	1010.9	1614.0	453.0	0.810	2.167
Toluene	0.37	857.8	1287.2	681.7	1.070	1.700
n-Butanol	1.66	802.5	1226.2	944.6	0.937	2.390

3. Results and discussion

The measured values of density ρ and sound velocity U and the calculated values of molar volume V, adiabatic compressibility β and the intermolecular free length L_f for the chosen binary mixtures are presented in Table 2.

Perusal of Table 2 indicates that the measured parameters in all the binaries increase non-linearly with the mole fraction of first component. This trend suggests the possibility of intermolecular interactions between the components of the systems [20]. The increasing trend of density reveals that the addition of first component makes the systems more compact, thereby revealing the attractive type interaction between the components. As the medium becomes more and more compact, velocity also increases as is observed in all the systems. Thus whether the components are polar or weak polar favourable interaction exists in all the system to make it compact is evident.

The same Table lists the calculated parameters of molar volume, adiabatic compressibility and the intermolecular free length of the experimental binary systems. It is interesting to note that these parameters, especially the molar volume, reflect specific variation with components of the mixture. The molar volume shows a continuous decrease in Aniline + Toluene system, a continuous increase in Toluene + n-Butanol system, but it first increases reaches a maximum at 0.2 mole fraction and then decreases in Aniline + n-Butanol system. Such variations predict that in the systems of Aniline + Toluene and Toluene + n-Butanol, though toluene is weak polar, the addition of polar molecule form some structural pattern. But if both components are polar as in Aniline + n-Butanol, the degree of interaction depends not only on the polarity or structure but some more factors. However, it is to be noted that the magnitude of molar volume are small as compared with the other two binaries, so that the medium is much more condensed in this system, only.

A monotonous decreasing nature of adiabatic compressibility (as well as inter molecular free length) is observed with increase in the mole fraction of first component in all the systems that assures that all systems shows structural compactness. However the degree of compactness differs from one system to other as is seen from the respective magnitude variations. Compressibility is the measure of the ease with which a system can easily be compressed. i.e., the larger the compressibility the easier it can be compressed because of more free space between the components [21]. Hence the observation of binary systems reveals that Toluene + n-Butanol & Aniline + n-Butanol systems are highly compressible whereas Aniline + Toluene system is less compressible.

Considering the two binary systems of toluene, it is evident that the aniline-toluene separation (or

Table 2. Measured and calculated values in chosen binaries at 303 K.

Mole fraction x_1	ρ (kgm^{-3})	U (ms^{-1})	V (x 10^6 m^3mol^{-1})	$\beta(\times 10^1$ $Pa^{-1})$	L_f (x10^{11} m)
Aniline + Toluene					
0.0000	857.8	1287.2	107.4143	6.5978	5.1252
0.0998	870.3	1324.3	105.9416	6.4168	5.0544
0.1992	884.6	1355.4	104.3703	6.2298	4.9802
0.3003	899.8	1388.6	102.7890	6.0327	4.9008
0.3997	916.2	1422.5	101.0353	5.8313	4.8182
0.5002	932.5	1454.6	99.3749	5.6201	4.7302
0.6013	947.2	1480.2	97.8886	5.3990	4.6362
0.7004	963.4	1512.4	96.4098	5.1760	4.5395
0.8002	981.2	1548.6	94.7046	4.9408	4.4351
0.9003	995.4	1585.5	93.5077	4.6985	4.3250
1.0000	1010.9	1614.0	92.1159	4.4455	4.2070
Aniline + n-Butanol					
0.0000	802.5	1226.2	92.3364	9.3432	6.0990
0.1000	820.6	1264.4	92.6266	8.8546	5.9373
0.1998	835.7	1303.3	93.2066	8.3665	5.7714
0.2999	858.3	1342.5	93.0397	7.8779	5.6003
0.4000	879.2	1386.9	92.9261	7.3868	5.4230
0.4989	901.5	1422.5	92.6400	6.9003	5.2413
0.6006	923.6	1460.7	92.5899	6.4042	5.0494
0.7001	946.4	1501.8	92.3746	5.9172	4.8536
0.8002	967.5	1535.6	92.3202	5.4260	4.6478
0.9003	986.2	1575.3	92.5227	4.9362	4.4331
1.0000	1010.9	1614.0	92.1159	4.4455	4.2070
Toluene + n-Butnaol					
0.0000	802.5	1226.2	92.3364	9.3432	6.0990
0.1008	806.4	1232.1	94.2184	9.0318	5.9965
0.1997	811.5	1238.0	95.7518	8.7346	5.8970
0.2995	816.3	1243.5	97.3699	8.4830	5.7977
0.3998	822.6	1250.2	98.8390	8.1585	5.6992
0.4987	826.4	1257.1	100.3911	7.8829	5.6021
0.6001	833.5	1263.2	101.8817	7.6121	5.5051
0.7006	839.6	1268.6	103.3715	7.3497	5.4093
0.8000	845.2	1274.2	104.7380	7.0934	5.3142
0.9001	852.4	1280.8	105.9892	6.8430	5.2195
1.0000	857.8	1287.2	107.4143	6.5978	5.1252

L_f) is smaller than the toluene-n-butanol separation. This suggests two different notions that either the toluene, if placed in a mixed environment of aniline and n-butanol, is likely to interact more with aniline or the structural pattern of the components make this variation. In general, alcohol molecules have both hydrophilic and hydrophobic groups, the later being denser than the former. The hydrophilic -OH group that

helps it dissolve polar molecules and ionic substances whereas the short, hydrophobic hydrocarbon chain can attract non-polar molecules [22]. Hence, n-butanol in spite of having two active groups and more polar than aniline, their hydrophilic part have no favourable counterpart to interact in the mixture of toluene whereas the hydrophobic part remains less interactive in aniline mixture. Thus the trend shown by the mixtures of n-butanol always make it to be highly compressible or higher separation between the components followed by increasing molar volume. This may be attributed to the inherent associative nature of the alcohol and in particular the excellent salvation nature of n-butanol. As the system is replaced by more polar molecules, depending on the other component of the system, either hydrophobic or hydrophilic interaction of increasing magnitude arises and hence adiabatic compressibility decreases [23, 24]. The same behaviour is reflected in intermolecular free length values.

Toluene and aniline being aromatic, and aniline with amino group, behave as electron donors. Though the amino group is comparatively a strong electron-donor, the H atoms in the NH_2 group can also play the role of electron-acceptor centre [25]. Hence toluene seems to behave only as electron-donor whereas aniline as donor and acceptor. Accordingly, the interactions of butanol, with its hydrophobic and hydrophilic groups, will be different depending on how the other component behaves. In the case of Toluene + Butanol binary, the hydrophobic group exhibits attractive type interactions and the hydrophilic shows repulsive type, so that the components cannot be treated very close to each other. However, in aniline-butanol mixture, both groups of butanol are counterbalanced by the donor and acceptor groups of aniline and hence possibilities are more to treat the components to be closer. This reassures the different observations made in the molar volume trend of the two binary systems and the decreasing nature of the same as found in Aniline + Butanol system.

Of the compressibility values of the Aniline + Toluene system, it is evident that aniline behaves as electron acceptor rather than electron donor. Thus it supports the dominating dipole or induced dipole type interactions of aniline with toluene rather than the inherent dispersive type of toluene. As dipole type interactions are stronger in magnitude than the other types, it is quite evident that the addition of aniline with toluene makes a structure formation.

The respective excess parameters have been calculated and are given in Figures 1 to 3. The deviation from ideality is an indication of the presence of interaction and the magnitude and sign of the parameters is a measure of interaction [26]. The +ve excess molar volume but the –ve compressibility and –ve free length found in Toluene + n-Butanol system confirms the existence of strong interactions in it. Thus all the parameters unanimously declare that among the binary systems considered here, the interactions in Toluene + n-Butanol system are found to be stronger while that of Aniline + Toluene is weaker.
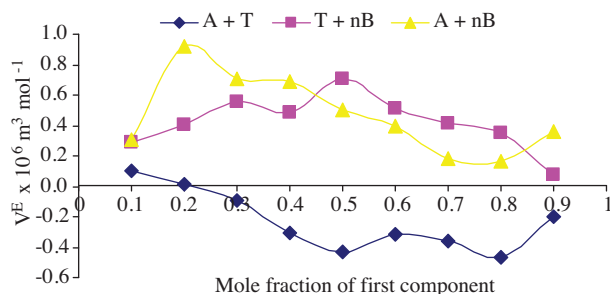

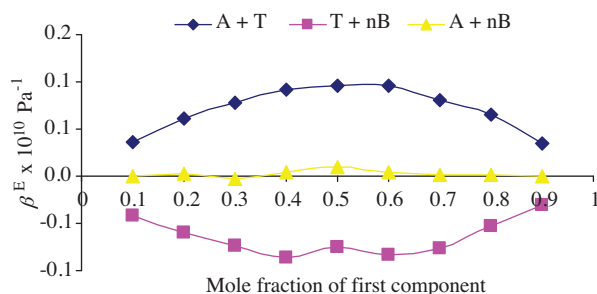**Figure 1.** Mole fraction *vs.* excess molar volume at 303 K.

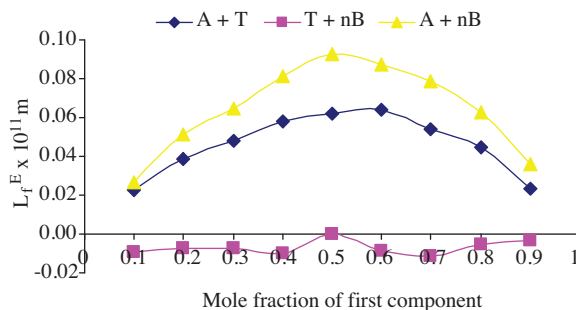**Figure 2.** Mole fraction *vs.* excess adiabatic compressibility at 303 K.

Figure 3. Mole fraction *vs.* excess intermolecular free length at 303 K.

To confirm the validity of these predictions, a variable degree Redlich-Kister polynomial in mole fractions was fitted to the results for each binary system by the statistically weighted least squares method using Marquardt algorithm. The algorithm itself optimizes n, the degree of polynomial. The expression has the form [27]

$$A^E = x_1(l - x_1)\Sigma A_n(l - 2x_1)^{n-1}, \tag{6}$$

where the summation extends from 1 to n. The coefficients of A, and the absolute error in the experimental excess property A^E are given in Table 3. R-K type equations belong to the category of orthogonal functions, which have a valuable feature that for a continuous series of observations (infinite) the values of the coefficients do not change as the number of terms in the series is increased. This is an important property because if a physical explanation can be assigned to one of its coefficients, its value remains constant. For the case of discrete measurements, such as the determination of molar volume of mixing, the values of coefficients will vary but very slightly. Tomiska [28, 29] provides the iteration formula as well as the proof that the procedure is independent of conversion coefficients from the actual excess property.

Table 3. Fitting Parameters for equation 6.

Quantity	A_0	A_1	A_2	A_3	χ^2	R^2
Aniline + Toluene						
V^Ex10^{-7}	-1.384 ± 0.169	1.397 ± 0.534	1.0290 ± 0.620	1.3680 ± 0.1318	0.01865	0.95421
β^Ex10^{-11}	0.384 ± 0.004	-0.065 ± 0.015	0.0183 ± 0.0149	0.0900 ± 0.0332	0.00004	0.99769
L_f^Ex10^{-12}	0.248 ± 0.003	-0.054 ± 0.013	0.0172 ± 0.0132	0.0758 ± 0.0292	0.00004	0.99572
Toluene + n-Butanol						
V^Ex10^{-7}	2.337 ± 0.182	-0.087 ± 0.064	-0.412 ± 0.064	2.322 ± 1.370	0.01252	0.94892
β^Ex10^{-11}	-3.305 ± 0.122	0.180 ± 0.046	-1.018 ± 0.461	-1.561 ± 1.044	0.00381	0.96881
L_f^Ex10^{-12}	-2.398 ± 0.339	2.381 ± 0.499	-1.257 ± 0.407	-1.071 ± 0.126	0.00772	0.97665
Aniline + n-Butanol						
V^Ex10^{-7}	2.077 ± 0.285	4.883 ± 1.037	1.997 ± 1.148	-6.790 ± 2.51	0.03197	0.98965
β^Ex10^{-11}	0.014 ± 0.007	-0.019 ± 0.022	-0.023 ± 0.016	0.035 ± 0.003	0.00265	0.99561
L_f^Ex10^{-12}	0.354 ± 0.006	-0.081 ± 0.021	-0.010 ± 0.021	0.033 ± 0.047	0.00008	0.97823

4. Conclusions

Presence of specific interactions is confirmed in all the systems. Aniline is found to readily influence the component molecules with its donor and acceptor groups. Further this work can be extended to continue the

analysis at different temperatures and more compositions.

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