Sound Velocities in Aqueous Solutions of n-Butylamine between 303.15 and 323.15 K: Experiment and Theory

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Abstract
Density (ρ) and sound velocity (u) have been measured for aqueous solutions of n-butylamine (W + NBA) in the whole range of composition at an interval of 5 K. Deviation in Sound Velocity (Δu), Isentropic Compressibility (Ks), Excess Isentropic Compressibility (KsE), Specific Acoustic Impedance (Z), Rao’s Constant (R) and Wada’s Constant (W) have been calculated from measured u and ρ. Δu versus x2 curve is negative and with the increment of temperature, Δu decreases; Ks values of W + NBA are all positive whereas KsE values are all negative. All the above outcomes are interpreted in terms of molecular interaction especially hydrogen bonding and hydrophobic hydration between water and n-butylamine. Moreover, experimental data for u correlated with some theoretical equations. The relations are Nomoto’s Relation (uN), Impedance Relation (uIR), Rao’s specific velocity method relation (uR), Van Deel’s ideal mixing relation (uIMR) and theoretical sound velocity according to Free Length Theory (uFLT). The validity of these relations with experimental values has been tested by measuring standard percentage deviation (SPD) and average percentage error (APE).

Keywords: Sound velocity, Isentropic compressibility, Hydrogen bonding, Hydrophobic hydration, Theoretical relations.

1. Introduction

Sound velocity provides valuable information about the physicochemical behavior of binary liquid mixtures. In 1945, Langemann and Dunbar showed qualitatively that the molecular association in liquids depends upon sound velocity [1]. Being related to the binding forces between the components of the medium, it is connected with the structure and molecular interactions existing in the liquid systems [2,3]. The derived properties such as adiabatic compressibility, excess isentropic compressibility, etc. provide a better understanding of the molecular scenario of liquids [4–8]. The sound velocity of the liquid mixture has significant applications in various industrial technological processes as it is useful to detect and evaluate molecular interactions [9–11].

The interaction between water and amines is quite complex. Both amines and water (W) are self-associated liquids through hydrogen bonding. Water forms trimer and larger aggregates of molecules by a cooperative interaction [12] and amine such as n-butylamine (NBA) are self-
associated to form non-cyclic trimer [13]. NBA possesses a hydrophilic amino (-NH\textsubscript{2}) group as well as a hydrophobic alkyl group. The nature of the interaction of these two groups toward water is completely different. The hydrophilic amino (-NH\textsubscript{2}) group interacts with water through H-bonding and disrupts normal water structure, while the alkyl group promotes the structure of water molecules through the hydrophobic hydration. It is believed that both effects take place in water-rich region.

Earlier, we reported excess molar volumes, viscosities, and refractive index of aqueous solutions of isomeric butylamines [14–16]. In the present communication, we are reporting some results related to sound velocities of W+NBA system in terms of experimental and theoretical approaches along with various acoustic and thermodynamic parameters. Moreover, to the best of our knowledge, they are scanty literature on this system. This investigation may serve as background work in formulating models for more complicated aqueous systems like surfactants, emulsions and biopolymers.

For the theoretical computation of sound velocity in liquid and liquid mixtures, several relations, semi-empirical formulas and theories are available in the literature. Among them, Nomoto’s Relation (\(u_N\)), Impedance Relation (\(u_{IR}\)), Rao’s specific velocity method relation (\(u_R\)), Van Deel’s ideal mixing relation (\(u_{IMR}\)) and Free Length Theory (\(u_{FLT}\)) are utilized to calculate sound velocities and then compared with experimental values [9,17–23].

2. Experimental section

2.1 Materials

\(n\)-butylamine (NBA) (purity = 99.5 %, mol. Wt. = 73.14 and B.P. = 78 °C) was procured from Sigma-Aldrich Chemical Co. Ltd and thrice distilled water was used for the preparation of an aqueous solution of \(n\)-butylamine. NBA was used without further treatment except keeping under molecular sieves (4Å) for 2-3 weeks prior to use.

2.2. Apparatus

The aqueous solutions at different compositions were made by volume using a pipette with an accuracy of ±0.01 cm\(^3\). Densities and sound velocities were measured by using the Anton Paar density meter (DSA 5000 M) with precision up to ±10\(^{-6}\) g.cm\(^{-3}\) and 0.1 m/s, respectively. The instrument was adjusted and calibrated with air and bi-distilled water at 293.15K maintaining the temperature constant up to ±0.01 K (density of air =0.001177 g.cm\(^{-3}\) and density of water = 0.998205 g.cm\(^{-3}\)).

2.3. Preparation of solutions

In order to measure sound velocity and density, binary solutions of water and NBA at different compositions were prepared by the volumetric method. Special caution was taken to prevent evaporation and also the introduction of moisture into the experimental samples.

The deviation in sound velocity, \(\Delta u\), is derived according to the following equation:

\[
\Delta u = u - (x_1 u_1 + x_2 u_2)
\]

Where, \(x_i\) and \(u_i\) are mole fraction and sound velocity of \(i^{th}\) component, respectively.

The isentropic compressibility, \(K_s\), is computed directly from the measured values of speed of sound and density using the Newton-Laplace equation:

\[
K_s = -\frac{1}{\rho_m} \frac{\delta \rho_m}{\delta P} = \left(\frac{1}{\rho u^2}\right) = \left(\frac{\rho}{\rho u^2}\right)
\]
Excess isentropic compressibility, $K_s^E$, is given by:

$$K_s^E = K_s - (\varnothing_1 K_{s1} + \varnothing_2 K_{s2})$$

In the above equation, $K_{s1}$ and $\varnothing_1$ are isentropic compressibility and volume fraction of $i$th component, respectively. Where, $\varnothing_i = \frac{x_i V_i}{\sum x_i V_i}$.

Specific acoustic impedance, $Z$, is determined from the equations:

$$Z = u \varrho$$

Rao’s constant and Wada’s constant is also a measure of interaction existing in the solution.

Rao’s constant, $R$, is calculated by using the following equation:

$$R = \frac{1}{u} V = \frac{1}{u_i} \frac{N}{\varrho}$$

Wada’s constant, $W_a$, is calculated by the following equation:

$$W_a = \frac{MK_s}{\varrho}$$

In order to correlate measured and some derived properties, the following general polynomial equations have been used:

$$Y = \sum_{i=1}^{n} a_i x_2^i$$

Here, $Y$ represents density, $\varrho$, $u_s$, $K_s$, $Z$, and $a_i$ is the fitting coefficient and $x_2$ is the mole fraction.

The excess or deviation parameters have been correlated by the Redlich-Kister polynomial equation of the form:

$$Z^E = x_2 (1 - x_2) \sum_{i=0}^{n} A_i (2x_2 - 1)^i$$

with the standard deviation, $\sigma$, following

$$(Z^E) = \left[ \frac{\sum (Z_{exp} - Z_{cal})^2}{n-p} \right]^{1/2}$$

Here, $Z^E$ represents $\Delta u$ and $K_s^E$, $Z_{exp}^E$ and $Z_{cal}^E$ are the experimental and calculated values of $Z^E$, respectively and $A_i$ is the i-th fitting coefficient, $n$ the number of measurements, $p$ the number of coefficients and the other terms have their usual significance.
2.4. Correlative models for sound velocity, \( u \)

2.4.1. Nomoto’s Relation \((u_{NR})\)

On assuming the additivity of molar sound velocity \((R)\) and no volume change on mixing, Nomoto established the following relation for the ultrasonic velocity of binary liquid mixtures:

\[
u_{NR} = \left( \frac{x_1 R_1 + x_2 R_2}{x_1 v_1 + x_2 v_2} \right)^{\frac{5}{2}}
\]

(10)

2.4.2. The Impedance Relation \((u_{IR})\)

Impedance is the product of ultrasonic velocity \((u)\) and the density \((\rho)\) of a liquid mixture. Hence, the impedance relation predicts the ultrasonic velocity of the given mixture by simply using the values of impedance \((Z_i)\) and the density \((\rho)\) values. Impedance relation is given as

\[
u_{IR} = \sum x_i Z_i
\]

\[
\rho_i
\]

Where \(x_i\) is mole fraction, \(\rho_i\) is the density of the mixture and \(Z_i\) is the acoustic impedance.

2.4.3. The Rao’s Specific Velocity Method Relation \((u_{R})\)

Rao’s specific velocity method is given as

\[
u_{R} = \left( \sum x_i r_i \rho_i \right)^{\frac{3}{2}}
\]

(12)

Where \(x_i\) is the mole fraction, \(u_i\) is the sound velocity and \(\rho_i\) is the density of the mixture. \(R_i\) is the Rao’s specific sound velocity, which is given by \(r_i = u_i \rho_i\) and \(Z_i\) is the acoustic impedance.

2.4.4. Ideal Mixing Relation based on Van Deel and Vangeel Theory

Van Deel and Vangeel proposed the ideal mixing theory in the light of assumptions made by Blandamer and Wadding, yield the following relation for adiabatic compressibility \((\beta_{ad})_{\text{mix}}\):

\[(\beta_{ad})_{\text{mix}} = (\beta_{ad})_1 + (\beta_{ad})_2 (\beta_{ad})_{\text{mix}}^2 \]

(13)

Where \(\phi_1\) and \(\phi_2\) are the volume fractions of the liquids 1 and 2, \(\gamma_1\) and \(\gamma_2\) are the ratios of specific heats of the respective liquids. This relation holds good if the mixture is ideal and if \(\gamma_1 = \gamma_2 = \gamma_{\text{mix}}\).

Using the additional assumption that \(V_1 = V_2\) the above equation can be transformed into a linear combination of mole fractions \(x_1\) and \(x_2\),

\[(\beta_{ad})_{\text{mix}} = x_1 (\beta_{ad})_1 + x_2 (\beta_{ad})_2 \]

(14)

On the basis of this equation, Van Deel and Vangeel obtained the relation for ultrasonic velocity in liquid mixtures as

\[
u_{IMR} = \left( \frac{x_1 R_1 + x_2 R_2}{x_1 v_1 + x_2 v_2} \right)^{\frac{3}{2}}
\]

(15)

Where \(u_1\) and \(u_2\) are the ultrasonic velocities of the pure liquid components.
2.4.5. Relation based on Free Length Theory

Jacobson deduced an empirical relation for ultrasonic velocity \((u_{FLT})\) making use of intermolecular free length \((L_f)\) and density \((\rho)\) as

\[
u_{FLT} = \frac{1}{K \cdot L_{mix} \cdot \rho_{mix}}
\]

(16)

Where \(K\) is temperature-dependent called Jacobson’s constant and the value of \(K\) at the working temperatures of the experiment were calculated (MKS units) and they are given below.

| Temperature (K) | 303.15 | 308.15 | 313.15 | 318.15 | 323.15 |
|-----------------|--------|--------|--------|--------|--------|
| Value of \(K\)  | 2.075x10\(^{-6}\) | 2.094x10\(^{-6}\) | 2.113x10\(^{-6}\) | 2.132x10\(^{-6}\) | 2.151x10\(^{-6}\) |

The Standard Percentage Deviation; \(\sigma\%\) for all mole fractions:

\[
\sigma\% = \left[ \frac{1}{n} \sum_{i=1}^{n} \left( \frac{(u_{exp} - u_{cal})}{u_{exp}} \right)^2 \right]^{\frac{1}{2}}
\]

(17)

Where \(n\) represents a number of data points [7].

2.4.6. The average percentage error (APE)

APE was calculated for the predicted refractive index data by the following equation

\[
APE = \frac{1}{n} \sum_{i=1}^{n} \left( \frac{(u_{mix})_{exp} - (u_{mix})_{cal}}{(u_{mix})_{cal}} \right) \times 100
\]

(18)

3. Results and discussion

Density \((\rho)\) and sound velocity \((u)\) were measured for the binary solutions of \(W + NBA\) in the whole range of composition at an interval of 5 K. Deviation in Sound Velocity \((\Delta u)\), isentropic compressibility \((K_s)\), excess isentropic compressibility \((K_s^E)\), specific acoustic impedance \((Z)\), Rao’s constant \((R)\) and Wada's constant \((W)\) were calculated from measured density \((\rho)\) and sound velocity \((u)\). Experimental data for \(u\) have been correlated with some theoretical equations. The relations are Nomoto’s Relation \((u_{N})\), Impedance Relation \((u_{IR})\), the Rao’s specific velocity method relation \((u_{R})\), Van Deel’s ideal mixing relation \((u_{IMR})\) and theoretical sound velocity according to Free Length Theory \((u_{FLT})\). Their validity was verified by measuring \(\sigma\%\) and APE.

3.1. Density \((\rho)\)

The densities, \((\rho)\) of the system \(W + NBA\) are shown in Table 1 and Figure 1(a) at different temperatures which are required to calculate some derived properties from sound velocity data. This time, we measured \(\rho\) by Anton Paar densitymeter (DSA 5000 M) instead of a pycnometer [14]. Though we changed the instrument, our present values agreed well with previous data. It can be seen from Figure 1(a) that the density decreases rapidly as NBA is added to water however with increasing concentration of NBA, the rate of fall of density decreases. At lower concentrations of NBA, the rate
of change of density with temperature appears to be much lower than the rate at higher concentrations of NBA [14].

Table 1: Densities, $\rho / \text{kg.m}^{-3}$ of W + NBA system for different molar ratios at different temperatures.

| $x_2$ | 303.15 K | 308.15 K | 313.15 K | 318.15 K | 323.15 K |
|-------|----------|----------|----------|----------|----------|
| 1.0000 | 727.3    | 722.6    | 717.6    | 712.7    | 707.8    |
| 0.8996 | 741.0    | 736.0    | 731.1    | 725.7    | 720.3    |
| 0.7991 | 754.1    | 749.3    | 744.5    | 739.7    | 733.9    |
| 0.6991 | 767.1    | 762.4    | 757.6    | 752.8    | 748.0    |
| 0.6014 | 782.7    | 778.1    | 773.8    | 768.7    | 762.3    |
| 0.4977 | 798.4    | 793.8    | 789.2    | 784.5    | 779.7    |
| 0.3970 | 818.1    | 813.7    | 809.2    | 804.7    | 800.1    |
| 0.2990 | 841.3    | 837.1    | 832.8    | 828.4    | 824.0    |
| 0.1992 | 875.0    | 871.1    | 867.1    | 863.1    | 859.0    |
| 0.0983 | 919.2    | 915.9    | 912.4    | 908.9    | 905.3    |
| 0.0000 | 995.7    | 994.1    | 992.2    | 990.3    | 988.1    |

3.2. Sound Velocity (u)

The sound velocities (u) of the systems W + NBA at different temperatures for different molar ratios are shown in Table 2 and plotted in Figure 1(b). The sound velocity of water is usually high. Sound velocity in water at 35°C and 45°C has been measured by plotting given data against temperature (The Engineering ToolBox, www.engineeringtoolbox.com). With the addition of amine in water, sound velocity decreases gradually from the water-rich region to the amine-rich region.

3.3. Deviation in Sound Velocity ($\Delta u$)

Deviation in sound velocities, ($\Delta u$) of W + NBA system at different temperatures are calculated according to Equation 1 and shown in Table 2 and plotted in Figure 1(c). The values of $\Delta u$ are fitted to the Redlich-Kister polynomial (Equation 8). The co-efficient of this equation along with Standard Deviations (Equation 9) are listed in Table 7. On examination of $\Delta u$ versus $x_2$ curve following characteristics are observed:

1) For W + NBA $\Delta u$ in $\Delta u$ versus $x_2$ curve is negative except at 303.15K temperature where at initial stage $\Delta u$ value rises slightly.
2) With the increment of temperature, $\Delta u$ value decreases.
3) For all the lines, they give minima and these minima shift from $x_2 \approx 0.2$ to $x_2 \approx 0.4$ with the rise in temperature.

Positive $\Delta u$ values indicate the experimental values are greater than those of the ideal one, i.e. to propagate sound waves and feel fewer obstacles. Whereas negative values of $\Delta u$ indicate more obstacles to propagating sound waves in the system which is observed in W + NBA system than that of ideal values. With the addition of butylamine, rowdiness due to intermolecular interaction increases. Hence, the value of $\Delta u$ decreases. As the temperature increases, the stability of H bonding between amine and water decreases. So, we observe the shifting of minima from lower temperature to higher temperature in the water-rich region.
Table 2: Sound velocities, u / m.s⁻¹ and deviation in sound velocities, ∆u / m.s⁻¹ of W + NBA system for different molar ratios at different temperatures.

| x₂   | u  | ∆u | u  | ∆u | u  | ∆u | u  | ∆u | u  | ∆u |
|------|----|----|----|----|----|----|----|----|----|----|
|      | 303.15 K |     | 308.15 K |     | 313.15 K |     | 318.15 K |     | 323.15 K |     |
| 1.0000 | 1221.10 | 0.0000 | 1212.56 | 0.0000 | 1204.62 | 0.0000 | 1196.79 | 0.0000 | 1188.14 | 0.0000 |
| 0.8996 | 1247.27 | -2.53436 | 1237.79 | -5.23538 | 1228.32 | -8.56655 | 1218.84 | -11.80588 | 1209.37 | -14.19714 |
| 0.7991 | 1272.63 | -5.90731 | 1262.16 | -11.36110 | 1251.55 | -17.63524 | 1241.26 | -23.27549 | 1230.60 | -28.42957 |
| 0.6991 | 1289.97 | -17.15731 | 1280.83 | -23.03510 | 1270.04 | -31.28324 | 1260.42 | -37.83649 | 1250.49 | -43.82557 |
| 0.6014 | 1312.60 | -22.45974 | 1301.58 | -31.93118 | 1288.56 | -44.16207 | 1278.85 | -52.35191 | 1265.37 | -63.42000 |
| 0.4977 | 1331.97 | -32.7357 | 1321.83 | -43.14791 | 1310.91 | -55.13917 | 1299.71 | -66.46058 | 1288.97 | -76.41158 |
| 0.3970 | 1361.85 | -31.64770 | 1350.65 | -44.88432 | 1339.42 | -58.99214 | 1327.22 | -72.90763 | 1316.74 | -84.17458 |
| 0.2990 | 1391.73 | -29.78590 | 1375.99 | -49.28144 | 1360.66 | -69.24738 | 1350.24 | -82.93421 | 1344.50 | -90.99486 |
| 0.1992 | 1432.24 | -17.80872 | 1418.41 | -37.14475 | 1391.64 | -57.27110 | 1379.70 | -75.18777 | 1379.70 | -91.01029 |
| 0.0983 | 1482.11 | 3.21397 | 1473.23 | -12.94185 | 1463.55 | -30.85835 | 1453.01 | -47.84226 | 1441.31 | -65.00386 |
| 0.0000 | 1507.00 | 0.0000 | 1516.00 | 0.0000 | 1526.00 | 0.0000 | 1534.00 | 0.0000 | 1541.00 | 0.0000 |

Table 3: Isentropic compressibility, kᵣ / 10⁻¹⁰Pa⁻¹ and excess isentropic compressibility, Kᵣᴱ / 10⁻¹⁰Pa⁻¹ of W + NBA system for different molar ratios at different temperatures.

| x₂   | Kᵣ | Kᵣᴱ | Kᵣ | Kᵣᴱ | Kᵣ | Kᵣᴱ | Kᵣ | Kᵣᴱ | Kᵣ | Kᵣᴱ |
|------|----|-----|----|-----|----|-----|----|-----|----|-----|
|      | 303.15 K |     | 308.15 K |     | 313.15 K |     | 318.15 K |     | 323.15 K |     |
| 1.0000 | 9.22113 | 0.0000 | 9.41230 | 0.0000 | 9.60322 | 0.0000 | 9.79619 | 0.0000 | 10.00816 | 0.0000 |
| 0.8996 | 8.67493 | -0.45181 | 8.86841 | -0.44532 | 9.06623 | -0.43425 | 9.27614 | -0.41334 | 9.49249 | -0.40506 |
| 0.7991 | 8.18744 | -0.82618 | 8.37706 | -0.81852 | 8.57498 | -0.80231 | 8.77482 | -0.78669 | 8.99765 | -0.76718 |
| 0.6991 | 7.83418 | -1.04232 | 7.99541 | -1.05691 | 8.18287 | -1.04499 | 8.36108 | -1.04518 | 8.54925 | -1.05443 |
| 0.6014 | 7.41549 | -1.29475 | 7.58627 | -1.29229 | 7.78327 | -1.26332 | 7.95475 | -1.26310 | 8.19303 | -1.21492 |
| 0.4977 | 7.05997 | -1.42422 | 7.21001 | -1.43222 | 7.37365 | -1.42627 | 7.54609 | -1.41530 | 7.71902 | -1.42217 |
| 0.3970 | 6.59048 | -1.60139 | 6.73672 | -1.59973 | 6.88811 | -1.59247 | 7.05482 | -1.57437 | 7.20874 | -1.58639 |
| 0.2990 | 6.13660 | -1.66170 | 6.30959 | -1.61487 | 6.48586 | -1.56417 | 6.62104 | -1.55996 | 6.71344 | -1.61380 |
| 0.1992 | 5.75185 | -1.63767 | 5.70588 | -1.60007 | 5.84434 | -1.55862 | 5.98244 | -1.52429 | 6.11549 | -1.50576 |
| 0.0983 | 4.95234 | -1.28158 | 5.03068 | -1.25297 | 5.11675 | -1.21494 | 5.21140 | -1.17729 | 5.31743 | -1.12751 |
| 0.0000 | 4.42240 | 0.0000 | 4.37713 | 0.0000 | 4.32787 | 0.0000 | 4.29145 | 0.0000 | 4.21924 | 0.0000 |
3.4. Isentropic Compressibility ($K_s$)

Isentropic Compressibility ($K_s$) of $W + NBA$ system was calculated by using Equation 2, tabulated in Table 3 and plotted in Figure 1(d). $K_s$ have been fitted to the general polynomial Equation 7. And the coefficients and regression values are given in Table 6. With close examination of the $K_s$ versus $x_2$ curves, the following characteristics have been observed.

Figure 1: (a) Densities, $\rho / \text{kg.m}^{-3}$, (b) Sound velocities, $u / \text{m.s}^{-1}$, (c) Deviation in sound velocities, $\Delta u / \text{m.s}^{-1}$ and (d) Isentropic compressibility, $K_s / 10^{-10} \text{Pa}^{-1}$ of $W + NBA$ system for different molar ratios at different temperatures. Solid lines represent polynomial fitting values.
1) Isentropic Compressibility values of W + NBA are all positive and gradually increase.
2) Initially, $K_s$ lines are twisted and after crossing this point $K_s$ lines are separated and rise gradually up to the whole mole fraction in amines.
3) $K_s$ values increase with the rise of temperature.

### 3.5. Excess Isentropic Compressibility ($K_s^E$)

Excess Isentropic Compressibility ($K_s^E$) of W + NBA was calculated at different temperatures by using Equation 3, tabulated in Table 3 and plotted in Figure 2(a). $K_s^E$ values have been fitted to the Redlich-Kister Equation 8. And the coefficients and standard deviations ($\sigma$%) are given in Table 7. On examination, $K_s^E$ versus $x_2$ curves give the following characteristics:

1) $K_s^E$ values are all negative.
2) Temperature effect is prominent at $x_2 \approx 0.1$ to $x_2 \approx 0.4$. It is negligible in extreme water-rich and amine-rich regions.

$K_s^E$ is nothing but the pressure dependence volume. The observed $K_s^E$ is negative. It indicates that these are less than ideal values. It is possible when the molecules comprising the systems are in a closer packing situation. With the addition of NBA to water, the solute can form hydrogen bonding of the type $N-H--------O$ (between the hydrogen atom of $-NH_2$ group of butylamine and the oxygen atom of $-OH$ group of a water molecule) leading to a contraction in volume which should result in negative $K_s^E$ values. In this volume contraction, the following factors are responsible:

1) Interstitial accommodation of molecules of one component into the structural network of the other component.
2) Favorable geometrical fittings.
3) Size differences of molecules.
4) Hydrophobic hydration is particularly important for these systems.

Considering the structural features and related properties of water and butylamines, high negative $K_s^E$ values are observed. Hydrophobic hydration plays the most important role which is in accord with the work of Saleh et. al [14].

### 3.6. Specific Acoustic Impedance (Z)

Specific Acoustic Impedance (Z) of W + NBA system was calculated at different temperatures by using Equation 4, tabulated in Table 4 and plotted in Figure 2(b). Z values have been fitted to the general polynomial Equation 7. The coefficients and regression values are given in Table 6. It is observed that the Z versus $x_2$ curve decreases with the addition of solute (butylamine). This behavior of acoustic impedance becomes responsible for the propagation of ultrasonic waves, and this behavior can be explained on the basis of hydrophobic interaction between water and butylamine. This behavior indicates the presence of strong molecular interaction by the addition of solute to water [24].

### 3.7. Rao’s Constant (R) and Wada’s Constant (Wa)

Rao’s Constant (R) and Wada’s Constant (Wa) of W + NBA system were calculated at different temperatures according to Equations 5 & 6 and listed in Table 5. And these have been plotted in Figures 2(c, d) respectively. R and Wa values have been fitted to the general polynomial Equation 7. And the coefficients and regression values are given in Table 6. It is observed that the lines increase
with the addition of butylamines to water up to the whole composition. And the curves increase with a slight curvature.

Figure 2: (a) Excess isentropic compressibility, $K^E/10^{-10}$ Pa$^{-1}$, (b) Specific acoustic impedance, $Z/\text{Pa.s.m}^{-1}$, (c) Rao’s constant, $R.10^4/\left(m^5.\text{mol}^{-1}.(m.s^{-1})^2\right)$ and (d) Wada’s constant, $Wa.10^3/\left(m^5.\text{mol}^{-1}.(N.m^{-2})^2\right)$ of W + NBA system for different molar ratios at different temperatures. Solid lines represent polynomial fitting values.
Table 4: Specific Acoustic Impedance, $Z / \text{Pa.s.m}^{-2}$ of W + NBA system for different molar ratios at different temperatures.

| $x_2$ | 303.15 K | 308.15 K | 313.15 K | 318.15 K | 323.15 K |
|-------|----------|----------|----------|----------|----------|
| 1.0000 | 88.8106  | 87.6196  | 86.4435  | 85.2952  | 84.0965  |
| 0.8996 | 92.4126  | 91.0976  | 89.7969  | 88.4767  | 87.1085  |
| 0.7991 | 95.9791  | 94.5788  | 93.1791  | 91.8119  | 90.3137  |
| 0.6991 | 98.9526  | 97.6489  | 96.2225  | 94.8905  | 93.5388  |
| 0.6014 | 102.7372 | 101.2746 | 99.7088  | 98.3001  | 96.4579  |
| 0.4977 | 106.3414 | 104.9273 | 103.4533 | 101.9604 | 100.5067 |
| 0.3970 | 111.4176 | 109.9028 | 108.3884 | 106.7999 | 105.3514 |
| 0.2990 | 117.0893 | 115.1816 | 113.3137 | 111.8570 | 110.7883 |
| 0.1992 | 125.3233 | 123.5594 | 121.8086 | 120.1143 | 118.5180 |
| 0.0983 | 136.2415 | 134.2821 | 133.5359 | 132.0616 | 130.4791 |
| 0.0000 | 150.0475 | 149.9095 | 151.4158 | 151.9044 | 153.8026 |

The values of Rao’s Constant (R) or Molar Sound Velocity and Wada’s Constant (Wa) or Molar Compressibility increase with concentration because of the presence of more molecules and thus leading to close packing of the medium. This thereby increases the interaction between solute and solvent [24].

3.8. Theoretical correlative model for Sound Velocity

In order to correlate the experimental sound velocity (u) value, different theoretical relations like Nomoto’s Relation ($u_N$) (Eqn. 10), The Impedance Relation ($u_{IR}$) (Eqn. 11), The Rao’s Specific Velocity Method ($u_R$) (Eqn. 12), Ideal mixing relation based on Van Deel and Vangeel theory ($u_{IMR}$) (Eqn. 15) and relation based on Free Length Theory ($u_{FLT}$) (Eqn. 16) were used. The correlating ability of each relation was tested by calculating standard percentage deviation ($\sigma$%), and average percentage error (APE) according to Equations 17 and 18 respectively. Experimental and different theoretical sound velocities ($u_{exp}$, $u_N$, $u_{IR}$, $u_R$, $u_{IMR}$ and $u_{FLT}$) at different temperatures were listed in Table 8 and plotted in Figure 3 for W + NBA system. The $\sigma$% and APE values for W + NBA system at different temperatures for different theoretical sound velocities has been presented in Tables 9, $\sigma$% values for W + NBA system are plotted in Figure 4. APE values for W + NBA system are shown in Figure 5. If the experimental value is more than the accepted value, we get a positive value of APE and a negative APE indicates that the experimental value is less than the accepted value.

It is observed from the tabulated values that the theoretical values of ultrasonic velocities evaluated by the above-mentioned relations show deviations from the experimental values. The reason for the deviation may be the limitations and approximations incorporated in these theories. In Nomoto’s Relation, the effect of volume change due to mixing was ignored i.e., the interaction between the molecules was not taken into the interpretation. In free length theory, it was anticipated that the molecular shape is spherical but it was not correct in all cases. In the case of ideal mixing relation, it was assumed that the ratio of specific heats and volumes are equal. Again molecular interactions were ignored. Also in the Impedance Relation ($u_{IR}$) and the Rao’s Specific Velocity Method ($u_R$) no molecular interactions were considered. Among them, sound velocities according to the Impedance Relation ($u_{IR}$) are the closest to the experimental values.

Upon mixing two liquids, the interaction between the molecules of the two liquids take place because of the presence of various types of forces such as dispersion forces, hydrogen bonding, dipole-dipole, dipole-induced dipole interactions and hydrophobic interaction. Thus, the observed deviation of theoretical values of velocity from the experimental values shows the molecular interactions between the unlike molecules in the liquid mixture.
Table 5: Rao’s constant, R. $10^4 / (m^2 \cdot mol^{-1} \cdot (m \cdot s^{-1})^{1/2})$ and Wada’s constant, Wa. $10^{1/2} / (m^2 / mol \cdot (N.m^{-2})^{1/2})$ of W + NBA system for different molar ratios at different temperatures.

| $x_2$ | R 303.15 K | W 308.15 K | R 313.15 K | W 318.15 K | R 323.15 K | W 328.15 K |
|-------|-----------|-----------|-----------|-----------|-----------|-----------|
| 1.0000 | 10.749 | 73.218 | 10.793 | 73.478 | 10.845 | 73.778 | 10.896 | 74.074 | 10.945 | 74.360 |
| 0.8996 | 10.625 | 72.494 | 10.670 | 72.759 | 10.715 | 73.018 | 10.766 | 73.320 | 10.819 | 73.625 |
| 0.7991 | 10.510 | 71.822 | 10.548 | 72.045 | 10.587 | 72.271 | 10.627 | 72.505 | 10.680 | 72.814 |
| 0.6991 | 10.379 | 71.055 | 10.419 | 71.286 | 10.454 | 71.496 | 10.494 | 71.729 | 10.534 | 71.963 |
| 0.6014 | 10.231 | 70.187 | 10.263 | 70.373 | 10.286 | 70.505 | 10.328 | 70.755 | 10.378 | 71.046 |
| 0.4977 | 10.080 | 69.293 | 10.112 | 69.483 | 10.143 | 69.667 | 10.175 | 69.852 | 10.208 | 70.050 |
| 0.3970 | 9.909 | 68.288 | 9.936 | 68.445 | 9.963 | 68.606 | 9.989 | 68.757 | 10.020 | 68.939 |
| 0.2990 | 9.706 | 67.086 | 9.718 | 67.159 | 9.732 | 67.240 | 9.758 | 67.395 | 9.797 | 67.622 |
| 0.1992 | 9.422 | 65.399 | 9.434 | 65.469 | 9.446 | 65.544 | 9.461 | 65.630 | 9.479 | 65.737 |
| 0.0983 | 9.072 | 63.309 | 9.087 | 63.400 | 9.101 | 63.486 | 9.115 | 63.566 | 9.126 | 63.636 |
| 0.0000 | 8.422 | 59.402 | 8.452 | 59.586 | 8.486 | 59.792 | 8.518 | 59.984 | 8.464 | 59.659 |

Table 6: Coefficients, $a_i$, of Equation 7, expressing densities, $\rho / kg \cdot m^{-3}$, sound velocities, $u / m \cdot s^{-1}$, isentropic compressibilities, $k_s / 10^{-10} P a \cdot s$, specific acoustic impedance, $z / Pa \cdot s \cdot m^{-1}$ and their regression indices, $R^2$ of W + NBA system for different molar ratios at different temperatures.

| Property | $T (K)$ | $a_0$ | $a_1$ | $a_2$ | $a_3$ | $a_4$ | $a_5$ | $R^2$ |
|----------|---------|-------|-------|-------|-------|-------|-------|-------|
| $\rho / kg \cdot m^{-3}$ | 303.15 | 0.9952 | -0.9462 | 2.2567 | -3.4620 | 2.7667 | -0.8833 | 0.9999 |
| 308.15 | 0.9936 | -0.9684 | 2.3277 | -3.5711 | 2.8424 | -0.9017 | 0.9998 |
| 313.15 | 0.9917 | -0.9872 | 2.3927 | -3.6677 | 2.9081 | -0.9182 | 0.9998 |
| 318.15 | 0.9897 | -1.008 | 2.4500 | -3.7557 | 2.9704 | -0.934 | 0.9998 |
| 323.15 | 0.9972 | -1.1741 | 3.2437 | -5.4360 | 4.5717 | -1.4952 | 0.9996 |
| $u / m \cdot s^{-2}$ | 303.15 | 1507.9 | -156.73 | -1851.2 | 4992.1 | -5011.7 | 1741.1 | 0.9995 |
| 308.15 | 1516.9 | -428.35 | -762.44 | 3116.8 | -3540.3 | 1310.4 | 0.9995 |
| 313.15 | 1526.9 | -734.32 | 594.02 | 476.18 | -1188.2 | 530.32 | 0.9994 |
| 318.15 | 1534.4 | -1004.8 | 1821.6 | -1933.8 | 959.35 | -180.06 | 0.9998 |
Table 7: Coefficients, \( A_i \), of Equation 8, expressing deviation in sound velocities, \( \Delta u / m \cdot s^{-1} \), excess isentropic compressibilities, \( K^E_s / 10^{-10} Pa^{-1} \), and standard deviation, (\( \sigma \)), Eqn. 9 of W + NBA system for different molar ratios at different temperatures.

| Property       | Property | T(K) | \( A_4 \) | \( A_5 \) | \( A_6 \) | \( A_7 \) | \( \sigma \) |
|----------------|----------|------|----------|----------|----------|----------|----------|
| \( \Delta u / m \cdot s^{-1} \) | 303.15 | -122.174 | 78.998 | 50.789 | 104.655 | 223.124 | -444.620 |
|                | 308.15 | -164.683 | 134.636 | -56.445 | 180.984 | 239.599 | -475.217 |
|                | 313.15 | -214.924 | 167.421 | -146.072 | 339.232 | 217.646 | -558.759 |
|                | 318.15 | -259.228 | 216.602 | -166.200 | 314.840 | 75.894 | -403.113 |
|                | 323.15 | -302.245 | 204.379 | -116.269 | 497.399 | -175.280 | -405.268 |
| \( K^E_s / 10^{-10} Pa^{-1} \) | 303.15 | -5.7770 | 3.2338 | -0.0010 | 1.5374 | -3.3356 | 3.9363 |
|                | 308.15 | -5.7999 | 3.0466 | -3.3355 | 1.2156 | -3.8560 | 4.5782 |
|                | 313.15 | -5.7555 | 3.1165 | -2.7276 | -0.0151 | -4.2901 | 5.9267 |
|                | 318.15 | -5.7345 | 1.9719 | -4.9871 | 2.6207 | 0.5359 | 4.5991 |
|                | 323.15 | -5.6927 | 3.6462 | -3.6153 | -2.0346 | -1.2556 | 6.8048 |
In statistics, the Standard Percentage Deviation (σ%) is used to measure quantitatively the amount of variation or dispersion of a set of data values. A low σ% indicates that the data points tend to be close to the mean. It is observed that σ% values and APE values of sound velocities according to the Impedance Relation (uIR) are the closest.

![Graphs showing sound velocities for different temperatures](image)

Figure 3: Experimental and different theoretical sound velocities, (uexpt, uN, uIR, uR, uIMR and uFLT) in m.s⁻¹, of W +NBA system for different molar ratios at different temperatures; (a) 303.15 K, (b) 308.15 K, (c) 313.15 K, (d) 318.15 K, and (e) 323.15 K.
Figure 4: Standard percentage deviation, $\sigma_\%$, for different theoretical sound velocities, ($u_N$, $u_{IR}$, $u_R$, $u_{IMR}$, and $u_{FLT}$) of W + NBA system at different molar ratios and different temperatures; (a) 303.15 K, (b) 308.15 K, (c) 313.15 K, (d) 318.15 K, and (e) 323.15 K.
Figure 5: Average percentage error, APE for different theoretical sound velocities, \(u_{n}, u_{ir}, u_{r}, u_{imr} \text{ and } u_{flt}\) of W + NBA system at different molar ratios and different temperatures.

Table 8: Experimental and different theoretical sound velocities, \(u_{\text{expt}}, u_{n}, u_{ir}, u_{r}, u_{imr} \text{ and } u_{flt}\) in \(m.s^{-1}\), of W + NBA system for different molar ratios at different temperatures.

| \(x_{2}\) | 303.15 K | 308.15 K | 313.15 K | 318.15 K | 323.15 K |
|---|---|---|---|---|---|
| \(u_{\text{expt}}\) | | | | | |
| 0.0000 | 1221.10 | 1212.56 | 1204.62 | 1196.79 | 1188.14 |
| 0.1000 | 1226.34 | 1194.98 | 1163.35 | 1132.88 | 1102.87 |
| 0.2000 | 1232.64 | 1201.92 | 1170.92 | 1140.98 | 1112.23 |
| 0.3000 | 1237.92 | 1210.38 | 1180.15 | 1150.86 | 1123.66 |
| 0.4000 | 1242.24 | 1220.69 | 1191.41 | 1162.92 | 1137.65 |
| 0.5000 | 1247.56 | 1230.92 | 1202.31 | 1173.62 | 1149.01 |
| 0.6000 | 1252.88 | 1241.24 | 1213.54 | 1185.03 | 1159.33 |
| 0.7000 | 1258.20 | 1251.56 | 1225.87 | 1197.48 | 1172.34 |
| 0.8000 | 1263.52 | 1261.90 | 1238.21 | 1210.72 | 1201.88 |
| 0.9000 | 1268.84 | 1272.24 | 1250.64 | 1223.15 | 1214.30 |
| 1.0000 | 1274.16 | 1282.56 | 1263.07 | 1235.58 | 1226.90 |
Table 9: Standard percentage deviation, $\sigma_{\%}(u)$ and average percentage error, APE for different theoretical sound velocities, $(u_{N0}, u_{IR}, u_{R}, u_{IMR}$ and $u_{FLT})$ in $m.s^{-1}$, of W + NBA system at different molar ratios and different temperatures.

| $x_2$ | $\sigma_{\%}(u_{N0})$ | $\sigma_{\%}(u_{IR})$ | $\sigma_{\%}(u_{R})$ | $\sigma_{\%}(u_{IMR})$ | $\sigma_{\%}(u_{FLT})$ |
|-------|----------------------|----------------------|----------------------|----------------------|----------------------|
| 0.1000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.01803 |
| 0.8996 | 0.01125 | 0.00820 | 0.01543 | 0.02173 | 0.01784 |
| 0.7991 | 0.01047 | 0.01085 | 0.02282 | 0.02943 | 0.01767 |
| 0.6991 | 0.01213 | 0.01384 | 0.03198 | 0.03585 | 0.01755 |
| 0.6014 | 0.01558 | 0.02076 | 0.03431 | 0.03629 | 0.01708 |
4. Conclusion

Sound velocity and density of W + NBA system were measured and various derived parameters, viz., Δu, K_s, K_s^E, Z, R and Wa (Wada’s Constant) were calculated. Here, it is found that with the addition of amine in water, sound velocity decreases gradually and Δu versus χ curve is negative except at 303.15 K temperature. It is also observed that K_s values are positive whereas K_s^E...
lines are negative. The variation of these properties with composition and temperature is explained through hydrogen bonding and hydrophobicity i.e. with the strength between constituents due to molecular interaction of the studied binary mixture. Without these five theoretical relations namely, Nomoto’s Relation ($u_{N}$), The Impedance Relation ($u_{IR}$), The Rao’s Specific Velocity Method ($u_{R}$), Ideal mixing relation based on Van Deel and Vangeel theory ($u_{IMR}$) and relation based on Free Length Theory ($u_{FLT}$) have been tested. The experimental and theoretical values of sound velocities correlated statistically through the standard percentage deviation ($\sigma$) and average percentage error (APE). From our analysis sound velocities according to the Impedance Relation ($u_{IR}$) is the best among the five relations.

Conflicts of Interest
The authors declare that there are no conflicts of interest regarding the publication of this paper.

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