Theoretical evaluation and comparative study of Ultrasonic velocities in binary liquid mixtures of Ethyl benzoate with some cresols at different temperatures


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ABSTRACT

Theoretical velocities of binary liquid mixtures of Ethyl benzoate (EB) with o-cresol (OC), m-cresol (MC) and p-cresol (PC), at T = (303.15, 308.15, 313.15, 318.15) K have been evaluated by theoretical models of the ultrasonic velocity determination are Nomoto (NOM), Impedance (IMP), Van Dael and Vangeel (VDV), Junjie’s (JUN) and Rao’s specific velocity (RAO) relations. Ultrasonic velocities and densities of these mixtures have also been measured experimentally as a function of composition of EB and temperature. A good agreement is found between experimental and theoretical values. $U_{exp}^2/U_{theo}^2$ has also been evaluated for non-ideality in the mixtures. Chi-square test for the goodness of the fit is applied to investigate the relative applicability of these theories to the present systems. The results are discussed in terms of intermolecular interactions between the component molecules in these binary liquid mixtures.

Keywords: Theoretical velocities, Ultrasonic velocities, Hydrogen bonding, Chi-square test, molecular interaction parameter.

INTRODUCTION

In the recent past, there is a rapid development on ultrasonic studies in various organic liquid mixtures [1-10] due to the fact that the optical methods cannot detect and assess all types of interactions, especially weak interactions in liquid mixtures. The important physicochemical properties like adiabatic compressibility, heat capacity, coefficient of expansion and critical temperature may be obtained from ultrasonic velocity, density and viscosity data. The molecular interactions in pure and binary liquid mixtures can be analyzed using ultrasonic velocity measurements which are of considerable interest for the physicists in the last few decades [11-21]. Using various theories [22-30] of ultrasonic sound velocities in liquid mixtures have been calculated and compared with experimental values.

The present work is a continuation of our research programme on a comparison of experimental ultrasonic velocity with the theoretical models of Nomoto, Impedance relation, Van Dael ideal mixing relation, Rao’s specific velocity and Junjie’s relation for the binary mixtures of several systems at various temperatures by our researchers. Of these models Nomoto relation holds good for the binary mixture at all temperatures under study. The results are interpreted in terms of intermolecular interactions between the binary component liquid mixtures [31-40].

In this paper we report the experimental and theoretical ultrasonic velocities of the binary liquid mixtures of Ethyl benzoate with o-cresol, m-cresol and p-cresol at 303.15, 308.15, 313.15, 318.15K over the entire composition range, evaluated by using various theories such as Nomoto (NOM), impedance (IMP), Van Dael and Vangeel (VDV), Junjie’s (JUN) and Rao’s specific velocity (RAO) relations. Further a comparative study of theoretical results with
experimental values using Chi-square test and the study of molecular interactions from the deviation ($\alpha$) in the value of $U^2_{\text{exp}} / U^2_{\text{im}}$ (from unity) have also been reported.

**EXPERIMENTAL SECTION**

The commercially available pure solvents were used in the present investigation EB (Merk > 99%) and OC, MC, PC of AR grade procured from S.D fine chemicals (India) were purified by the standard methods described by A. Weissberger [41] and the purity of the chemicals was assessed by comparing their measured densities ($\rho$) and ultrasonic velocities ($U$) which were in good agreement with literature values. The mixtures were prepared gravimetrically using an electronic balance (Shimadzu AY120) with an uncertainty of $\pm 1 \times 10^{-7}$ Kg and were stored in air-tight glass bottles. The uncertainty in the mole fraction was estimated to be less than $\pm 1 \times 10^{-4}$. It was ensured that the components were adequately mixed before being transferred into the apparatus. The required properties were measured within one day of the mixture preparation.

The densities, $\rho$, of pure liquids and their mixtures are determined using a $10^{-5}$ m$^3$ Double - arm pycnometer, and the values from triplicate replication at each temperature are reproducible within $2 \times 10^{-1}$ kg m$^{-3}$ and the uncertainty in the measurement of density is found to be 2 parts in 10$^4$ parts. The reproducibility in mole fractions was within $\pm 0.0002$. Temperature control for the measurement of viscosity and density is achieved by using a microprocessor assisted circulating water bath, (supplied by Mac, New Delhi) regulated to $\pm 0.01$ K, using a proportional temperature controller. Adequate precautions were taken to minimize evaporation losses during the actual measurements. The ultrasonic velocity of sound ($U$) is measured using an ultrasonic interferometer (Mittal Enterprises, New Delhi model F05) operating at 2MHz. The measured speeds of sound have a precision of 0.8 m. sec$^{-1}$ and an uncertainty less than $\pm 0.1$ m. sec$^{-1}$. The temperature stability was maintained within $\pm 0.01$ K by circulating water bath around the measuring cell through a pump.

**Theoretical considerations:**

1. **Nomoto theory:** Nomoto’s empirical formula is based on the assumption of the linear dependence of the molecular sound velocity on concentration and the additivity of the molar volume in the liquid mixture. The sound velocity $U$ is given by

$$U = \left( \frac{\sum x_i R_i}{\sum x_i V_i} \right)^{\frac{3}{2}}$$

Where the molar sound velocity $R = x_i R_i + x_2 R_2$

Hence, ultrasonic velocity ($U$) is given by

$$U = \left( \frac{x_i R_i + x_2 R_2}{x_v V_1 + x_2 V_2} \right)^{\frac{3}{2}}$$  

......... (1)

In the above equation $R_i = (M_i/\rho_i) U_i^{1/3} = V_i (U_i)^{1/3}$

1.2 **Impedance relation:** The specific acoustic impedance of the pure liquids is used for evaluating the ultrasonic velocity in the liquid mixtures by the following relation:

$$U = \sum x_i Z_i / \sum x_i$$  

......... (2)

Where $Z_i$ is acoustic impedance and $\rho_i$ is the density of the mixture.

1.3 **Van Dael and Vangeel relation:** Van Dael and Vangeel obtained the formula for ultrasonic velocity in the liquid mixtures adopting the adiabatic compressibilities of the pure liquids based on ideal mixing of the liquids. Van Dael and Vangeel assumed that the adiabatic compressibility ($\beta_{\text{ad}}$) of the mixture is given by

$$\beta_{\text{ad}} = \phi_A (\beta_{\text{ad}})_A + \phi_B (\beta_{\text{ad}})_B$$

and suggested the following relation for sound velocity in homogeneous liquid mixtures.

$$\beta_{\text{ad}}^{\text{im}} = \phi_A \gamma_A (\beta_{\text{ad}})_A + \phi_B \gamma_B (\beta_{\text{ad}})_B$$

Where $\phi$ and $\gamma$ refer the volume function and principal specific ratio.
It holds true if the mixture is an ideal one and also $\gamma_A = \gamma_B = \gamma_{im}$. It can be transformed into a linear combination of the mole fractions if the additional assumption $v_A = v_B$ is made

$$\beta_{ad}^{im} = x_A(\beta_{ad})_A + x_B(\beta_{ad})_B$$

The sound velocities appropriate to the above equations are given by

$$\frac{x_AV_A + x_BV_B}{x_AM_A + x_BM_B} = \left( \frac{U}{U_{im}} \right)^2 = \varphi_A \frac{V_A}{M_AU_A} + \varphi_B \frac{V_B}{M_BU_B}$$

and

$$\frac{x_AM_A + x_BM_B}{x_BM_B} = \left( \frac{U}{U_{im}} \right)^2 = \frac{x_A}{M_AU_A} + \frac{x_B}{M_BU_B}$$

(3)

**1.4 Junjie’s relation:** This relation derived by Junjie’s for the ultrasonic velocity of the mixture in terms of the mole fraction, molecular weight and density of the mixture.

$$U = \frac{\sum_{i=1}^{n} x_iV_i}{\sum_{i=1}^{n} x_iM_i^{1/2} / \left( \sum_{i=1}^{n} x_iV_i / \rho_i U_i^{2} \right)^{1/2}}$$

(4)

where the symbols have their usual meanings.

**1.5 Rao’s relation:** Using the ratio of the temperature coefficient of velocity and expansion coefficient, Rao derived a formula for ultrasonic velocity ($U$)

$$U = C \left( \frac{R}{V} \right)^3$$

(5)

where $V$ is the molar volume and $R$ is called Rao’s constant or molar sound velocity, which is constant for a liquid at a temperature.

**Chi-square test for goodness of fit:**

According to Karl Pearson, Chi-square value is evaluated for the binary liquid mixtures under study using the formula

$$\chi^2 = \sum_{i=1}^{n} \left( \frac{U_{(obs)} - U_{(cal)}}{U_{(cal)}} \right)^2$$

(6)

where $n$ is the number of data used,

and $U_{(obs)}$ = experimental values of ultrasonic velocities

$U_{(cal)}$ = computed values of ultrasonic velocities

**Relative percentage of error ($\sigma$):**

The Average percentage error is calculated by using the relation

$$\sigma = \frac{1}{n} \sum \left( \frac{U_{(obs)} - U_{(cal)}}{U_{(obs)}} \right) \times 100\%$$

(7)

Where $n$ is the number of data used,

$U_{(obs)}$ = experimental values of ultrasonic velocities

$U_{(cal)}$ = computed values of ultrasonic velocities

**Molecular associations:**

The degree of intermolecular interaction or molecular association is given by

$$\alpha = \left[ \frac{U_{exp}^2}{U_{mix}^2} \right] - 1$$

(8)
RESULTS AND DISCUSSION

The experimental ultrasonic velocities and the theoretical values evaluated by Nomoto’s Relation (NOM), Impedance Relation (IMP), Van Deal and Vangeel Ideal Mixing Relation (VDV), Junjie’s relation (JUN), Rao’s specific velocity method (RAO) are compared for all the three binaries Ethyl benzoate + o-cresol, Ethyl benzoate + m-cresol and Ethyl benzoate + p-cresol along with the percentage of deviations are presented in TABLES 1-3 at all the four temperatures 303.15, 308.15, 313.15, 318.15 K and atmospheric pressure. The validity of different theoretical formulae is checked by the chi-square test for all the mixtures at all the temperatures and the values are given in TABLE-4.
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**TABLE-2**

Experimental and theoretical values of velocities with their % deviation for the system (Ethyl benzoate + m-cresol)

**AT 303.15K**

**AT 308.15K**

**AT 313.15K**

**AT 318.15K**
| $\alpha$  | EXP | NOM | IMP | VDV | JUN | RAO | %NOM | %IMP | %VDV | %JUN | %RAO | %NOM | %IMP | %VDV | %JUN | %RAO |
|---------|-----|-----|-----|-----|-----|-----|------|------|------|------|------|------|------|------|------|------|------|
| 0.0000  | 1469.1 | 1469.1 | 1469.1 | 1469.1 | 1469.1 | 1469.1 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 0.0749  | 1460.2 | 1456.5 | 1459.8 | 1456.0 | 1455.4 | 1461.9 | -0.25 | -0.03 | -0.29 | -0.33 | 0.11 | 0.0058 |
| 0.1541  | 1450.7 | 1444.0 | 1450.0 | 1442.9 | 1442.1 | 1453.9 | -0.47 | -0.05 | -0.54 | -0.59 | 0.22 | 0.0108 |
| 0.2380  | 1440.6 | 1431.5 | 1439.6 | 1430.0 | 1429.1 | 1444.9 | -0.63 | -0.07 | -0.74 | -0.80 | 0.30 | 0.0149 |
| 0.3270  | 1429.8 | 1419.1 | 1428.6 | 1417.2 | 1416.4 | 1435.1 | -0.75 | -0.09 | -0.89 | -0.94 | 0.36 | 0.0179 |
| 0.4216  | 1418.3 | 1406.8 | 1416.9 | 1404.6 | 1404.0 | 1424.0 | -0.81 | -0.10 | -0.97 | -1.01 | 0.40 | 0.0196 |
| 0.5223  | 1406.0 | 1394.5 | 1404.5 | 1392.2 | 1391.9 | 1411.7 | -0.81 | -0.10 | -0.98 | -1.00 | 0.41 | 0.0199 |
| 0.6297  | 1392.7 | 1382.3 | 1391.3 | 1380.1 | 1380.1 | 1398.0 | -0.74 | -0.10 | -0.90 | -0.90 | 0.38 | 0.0183 |
| 0.7446  | 1378.4 | 1370.2 | 1377.3 | 1368.3 | 1368.5 | 1382.7 | -0.59 | -0.08 | -0.73 | -0.71 | 0.31 | 0.0147 |
| 0.8677  | 1362.9 | 1358.2 | 1362.3 | 1357.0 | 1357.2 | 1365.5 | -0.35 | -0.05 | -0.43 | -0.42 | 0.19 | 0.0088 |
| 1.0000  | 1346.2 | 1346.2 | 1346.2 | 1346.2 | 1346.2 | 1346.2 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.0000 |

**Table 3**

Experimental and theoretical values of velocities with their % deviation for the system (Ethyl benzoate + p-cresol) at different temperatures.
Table 4: Values of chi-square and sigma relative deviation for all the binary mixtures of Ethyl benzoate at different temperatures.

| Temperature (K) | NOM | IMP | VDV | JUN | RAO | NOM | IMP | VDV | JUN | RAO | NOM | IMP | VDV | JUN | RAO |
|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 303.15          | 0.67| 0.01| 0.70| 1.11| 0.00| 0.062| 0.005| 0.064| 0.081| 0.004|
| 308.15          | 0.62| 0.02| 0.67| 1.03| 0.01| 0.060| 0.004| 0.063| 0.078| 0.009|
| 313.15          | 0.61| 0.01| 0.63| 1.03| 0.02| 0.060| 0.003| 0.061| 0.078| 0.010|
| 318.15          | 0.63| 0.01| 0.61| 1.09| 0.03| 0.062| 0.002| 0.060| 0.081| 0.013|

Fig (a): Plots of $U_{exp}^2/U_{imx}^2$ vs $X_1$ for the studied system EB+OC, at temperatures 303.15K, 308.15K, 313.15K and 318.15K.

Fig (b): Plots of $U_{exp}^2/U_{imx}^2$ vs $X_1$ for the studied system EB+MC, at temperatures 303.15K, 308.15K, 313.15K and 318.15K.
The values of ultrasonic velocity computed by various theories along with experimental values (U) are given in TABLES 1-3. There are variations between the evaluated and experimental values. Data reveals that the velocities computed from Impedance relation (IMP) and Rao’s specific velocity model exhibit more satisfactory agreement with the experimental values in the temperature range 303.15K to 318.15K than other approaches in the binary systems. The agreement between theoretical velocities of Impedance relation and Rao’s specific velocity relation in all the three binary systems studied. It is observed that the experimental values show deviation with the theoretical values of ultrasonic velocities which confirms the existence of molecular interactions [42]. This may be due to interactions occurring between the hetero molecules of the binaries. From the observed values of all the three systems, there is a good agreement between theoretical and experimental values through Impedance Relation followed by Rao’s specific velocity relation. However, higher deviations are observed in Van Deel and Vangeel, Nomoto’s relation and slight variations in Junjie’s relation. There are higher variations in some intermediate concentration range suggesting the existence of strong tendency of association between component molecules as a result of hydrogen bonding. Nomoto’s theory proposes that the volume does not change upon mixing. Therefore, no interaction between the components of liquid mixtures has been taken into account. Similarly, the assumption for the formation of ideal mixing relation is that, the ratios of specific heats of ideal mixtures and the volumes are also equal. Again no molecular interactions are taken into account. But upon mixing, interactions between the molecules occur because of the presence of various types of forces such as dispersion forces, charge transfer, hydrogen bonding dipole-dipole and dipole-induced dipole interactions. Thus, the observed deviation of theoretical values of velocity from the experimental values shows that the molecular interactions are taking place between the unlike molecules in the liquid mixtures. From the Tables it is observed that maximum positive deviation at 0.5 mole fraction of all the 3 systems at all the temperatures. The ratio \( U_{2}^{\text{exp}}/U_{2}^{\text{imx}} \) is an important tool to measure the non ideality in the mixtures especially in such cases where the properties other than sound velocity are not known.

Figures a, b and c represent the variation of \( U_{2}^{\text{exp}}/U_{2}^{\text{imx}} \) with the mole fraction of EB for all three binary systems studied, and the ratio of \( U_{2}^{\text{exp}}/U_{2}^{\text{imx}} \) gives an idea of extent of interaction taking place between molecules of the mixtures. It is positive for three systems and infers strong interactions between the components. The percentage of deviation in velocity is reflecting both negative and positive magnitudes, indicating non ideal behaviour of liquid mixtures. The evaluated interaction parameters are positive for all the systems, indicating stronger interactions between the mixing molecules, which increase from o-cresol to p-cresol. This suggests somewhat stronger interaction of EB with p-cresol in comparison to other components. The negative values indicate the dominance of dispersion forces arising from the breakage of hydrogen bonds in the associates. But a positive value of (\( \alpha \)) in all the system clearly indicates the existence of strong tendency for the formation of association in mixture through dipole-dipole interactions higher values of percentage deviation indicates maximum departure of the particular theory from experiment at that particular concentration and magnitude of the chi-square value finally determines the overall validity of the theory. The chi square values along with average percentage error are given in TABLE- 4.

CONCLUSION

From the values of experimental and evaluated velocity values, it may be concluded that, the Impedance Relation followed by Rao’s specific velocity relation of Ultra sound velocity have provided good results. Thus, the linearity of molar sound velocity and additivity of molar velocities, as suggested by Impedance Relation and Rao’s specific velocity relation in deriving the empirical relations have been truly observed in the aforementioned binary liquid
mixtures. The success of these relations in predicting the experimental ultrasonic velocities for polar-polar liquid mixtures has also been emphasized by others.

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