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Comparison of Theoretical Ultrasonic Velocities in Binary Liquid Mixture Containing α-Picoline in Ethanol

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ABSTRACT

The ultrasonic velocity and related acoustical parameters are the important tools in understanding the nature and extent of pattern of molecular association resulting from intermolecular interactions between components of liquid mixture. These parameters have been used to understand different kinds of association, molecular packing and various types of intermolecular interactions and their strength of influence by the size of pure components and their mixture. Measurement of ultrasonic velocity gives the valuable information about the physico-chemical behavior of liquids and their mixtures. The theoretical evaluations of ultrasonic velocities in these pure liquids and binary liquid mixture and its comparison with measured values predict the extent of intermolecular interactions in the liquid mixture. The statistical and thermodynamic theories have been used to compute ultrasonic velocity in binary liquid mixture containing α- picoline in ethanol over the whole concentration range at 301.15K. Collision factor theory Nomato's relation, Van Deel's ideal mixing relation and Junji's relation are used to compute theoretical ultrasonic velocities .These values are compared with the experimental values and their validity are checked by calculating the average percentage error. The agreement between theoretical and of experimental values was found to be satisfactory. Further, the molecular interaction parameter (α) was computed by using the values of experimental and theoretical ultrasonic velocities. The variations of this parameter with composition of mixture indicate the existence of molecular interactions in binary liquid mixture. The collision factory theory proposed by Shaft and Nutsch-Kuhnkies is found to best suited with experimental values having minimum percentage error over whole concentration range

Key words: theoretical ultrasonic velocities, binary liquid mixture, α- picoline in ethanol, molecular interaction parameter, average percentage error, Nomato's relation, VanDeel's ideal mixing relation, Junji's relation and collision factor theory**.**

INTRODUCTION

Ultrasonic study of pure liquids and liquid mixtures has much importance during last two decades to investigate the nature of molecular interactions in the binary liquid mixtures. Ultrasonic velocity is a highly sensitive parameter to the structure and interactions exists in pure liquids and their mixtures and it is fundamentally related to binding forces between constitutes of liquids Ultrasonic velocity is probably the best measure for the mechanical stability of liquids and their mixtures. Ultrasonic velocity has been employed to identify the conformational transition from native to denatured states of bio-molecules and macromolecules'. Measurement of ultrasonic velocity gives the valuable information about the physico-chemical behavior of liquids and their mixtures [1-4]. Several relations and semi-empirical formulas and theories are available for theoretical computation of ultrasonic velocity in pure and

liquid mixtures [**5-7**] and widely used in processing and product formation in many industrial applications. Thermodynamic and transport properties of liquids provides the useful information about physical forces acting between the molecules of same substance i.e. pure liquids and of different substances of liquid mixtures. When two liquids are mixed together, the resulting changes in physical and thermodynamic properties can be considered as a sum of several contributions due to change in free volume, change of entropy, change in energy and change in a molecular orientation.

Theoretical evaluation of ultrasonic velocity in pure and liquid mixtures and their comparison with experimental values reflects the molecular interactions and used to build comprehensive theoretical model for fluids. Successful attempt has been made in recent years on theoretical computation of ultrasonic velocity in pure and liquid mixtures using semi empirical, statistical thermodynamic theories. The ultrasonic velocity in pure liquids and their mixtures have been computed by using Nomato's relation[8], Van Deel and Vangeel ideal mixing relation[9-10], Junjies relation[11] , Impedance dependence relation and collision factor theory[12-13].

MATERIALS AND METHODS

The chemicals α- picoline and ethanol used were of analytical grade and obtain from Merck chemicals private Ltd. (Purity 99.5%). The densities of pure components and binary mixtures were measured by hydrostatic sinker method with an accuracy 1 part in10^{+5}. Special attention was given to avoid the vaporization of solution. Comparing with their density with literature values checked the purity of chemicals. The mixtures of various concentrations in mole fraction were prepared. The ultrasonic velocities in pure liquids and their mixtures have been measured by pulse echo-overlap technique (PEO) using ultrasonic time intervalometer (UTI-101) supplied by M/s Innovative Instruments Ltd. Hyderabad at a central frequency of 10 MHz with accuracy ± 0.01 m/s. The viscosity of pure and mixture is measured by an Ostwald's Viscometer with accuracy ± 0.001 $\mathrm{Nm^{-2}s}$. The temperature of pure liquids and their mixtures is maintained constant with the help of thermostat U-10 with an accuracy of ± 0.01K.

1. Theory:

Nomato establish the relation for ultrasonic velocity in a binary liquid mixtures on the assumption of additivity of molar sound velocity with concentration of molar fraction as

$$u_{\text{Nomato}} = \left[\frac{x_1R_1 + x_2R_2}{x_1V_1 + x_2V_2}\right]^3 \qquad (1)$$

where $R_1 = \dfrac{M_1u_1^{1/3}}{\rho_1}$, $R_2 = \dfrac{M_2u^{1/3}}{\rho_2}$ and $V_1 = \dfrac{M_1}{\rho_1}$, $V_2 = \dfrac{M_2}{\rho_2}$

In above equations x_1 and x_2 are the mole fraction of component liquids. M_1, M_2, u_1, u_2, V_1 and V_2 are the molecular weights, ultrasonic velocity and molar volumes of components of binary liquids mixtures.

The ideal mixing theory proposed by VanDeel and Vangeel using the assumptions made by Balndamer and Waddington yields the relation for compressibility,

$$\beta_{\text{ad}} = \phi_1\left(\frac{\gamma_1}{\gamma_{mix}}\right)(\beta_{ad})_1 + {}_2\left(\frac{\gamma_2}{\gamma_{mix}}\right)(\beta_{ad})_2 \qquad (2)$$

where φ_1 and φ_2 are the volume fraction of the components of liquid mixture and γ_1 and γ_2 are the ratio of specific heats of respective components respectively. Using additional assumptions this equation can be written as

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

Using this relation VanDeel obtained the expression for ultrasonic velocity in binary liquid mixture as

$$\left[\frac{1}{x_1M_1 + x_2M_2}\right]\frac{1}{u_{mix}^2} = \frac{x_1}{M_1u_1^2} + \frac{x_2}{M_2u_2^2} \qquad (3)$$

where u_1 and u_2 are the ultrasonic velocity in binary liquid mixture and u_{mix} is an ideal mixing ultrasonic velocity in liquid mixture.

The Junjie's relation for determination of ultrasonic velocity in binary liquid mixture can be given as

$$U_{JR} = \left[\frac{1}{x_1M_1 + x_2M_2}\right]^{1/2} * \left[\frac{x_1}{M_1u_1^2} + \frac{x_2}{M_2u_2^2}\right]^{-1/2} \qquad (4)$$

Symbols have their usual meaning.

Shaft and Nutsch-Kuhnkies [14] developed the collision factor theory (CFT) for evaluation of ultrasonic velocity in binary liquid mixture as

$$u_{CFT} = u_\alpha\left[\frac{(x_1S_1 + x_2S_2)(x_1B_1 + x_2B_2)}{V_m}\right] \qquad (5)$$

Where $V_m = \dfrac{x_1M_1 + x_2M_2}{\rho_{mix}}$ $\quad B = \dfrac{4}{3}\pi \cdot Nr^3$ and $r = \left(\dfrac{3b}{16\pi \cdot N}\right)^{1/3}$

$$b = \left(\frac{M}{\rho}\right)\cdot\left[1 - \frac{RT}{Mu^2}\left(\sqrt{\frac{1 + Mu^2}{3RT}} - 1\right)\right] \quad \text{and} \quad u_\alpha = 1600 \text{ m/s}$$

The ultrasonic velocity in binary liquid mixture is also given by Impedance dependence relation,

$$u_{IDR} = \frac{x_1Z_1 + x_2Z_{2_1}}{x_1\rho_1 + x_2\rho_2} \qquad (6)$$

Where $Z_1 = u_1.\rho_1$ and $Z_2 = u_2.\rho_2$

The molecular interaction parameter (α) is expressed as

$$\alpha = \left[\left(\frac{u_{expt}}{u_{Theo}}\right)^2 - 1\right] \qquad (7)$$

RESULTS AND DISCUSSION

The theoretically computed values of ultrasonic velocities by using Nomato's empirical formula, VanDeel and Vangeel expression based on Richardson's assumptions, Junjie method, Impedance dependence relation and collision factory theory with experimental values are presented in Table-I over whole concentration range of α-picoline in ethanol at 301.15K.

The molecular interaction parameter (MIP) and percentage deviation of ultrasonic velocity is summarized in Table-II and Table-III respectively. The validity of these theories is checked by applying Chi-square test and average percentage error.

According to Karl Pearson the chi-square value is calculated by using relation

$$x^2 = \frac{[(u_{mix})_{Expt} - (u_{mix})_{Theo}]}{(u_{mix})_{Theo}}$$

The average percentage error (APE) is calculated by using relation

$$APE = \frac{1}{n}\sum \left[\frac{[(u_{mix})_{Expt} - (u_{mix})_{Theo}]}{(u_{mix})_{Theo}}\right] \times 100$$

Where *n* be the number of values of ultrasonic velocity, $(u_{mix})_{expt}$ and $(u_{mix})_{Theo}$ are the experimental and theoretical values of ultrasonic velocities in binary liquid mixture
[15-17].

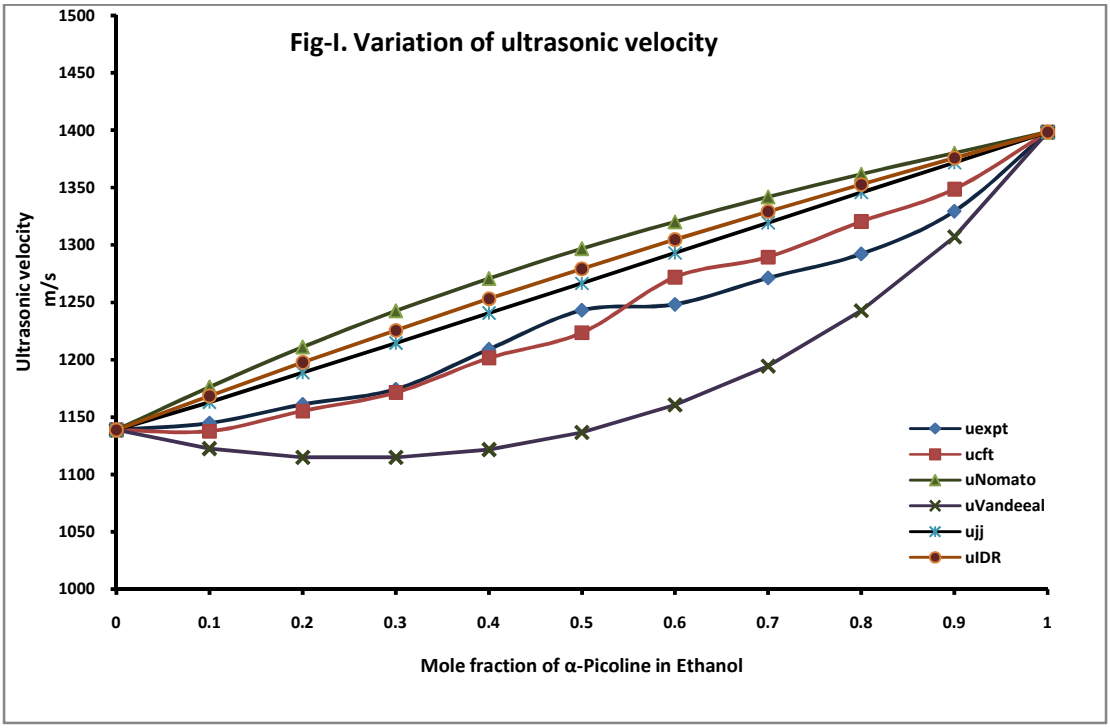
When two liquids are mixed together, the interaction between the molecules of two liquids takes place because of the presence of various forces like a dispersive force, charge transfer, hydrogen bonding and dipole induced dipole interactions. Therefore deviation is observed in calculated values from experimental values of ultrasonic velocities [18-24].

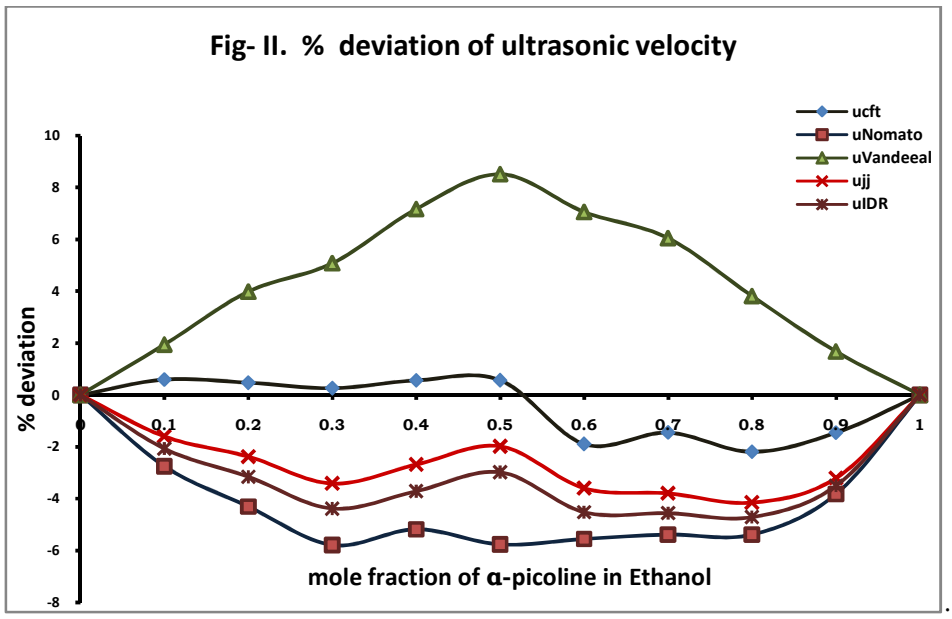
Table- I: Experimental and theoretical velocity u_{expt} , u_{cft}, u_{Nomato}, u_{jj} and u_{IDR}, using collision factory theory, Nomato's empirical formula, VanDeel and Vangeel's expression, Junjie's method and Impedance dependence relation.

Mole Fraction(*x*)	u_{expt} m/s	u_{cft} m/s	u_{Nomato} m/s	$u_{Vandeeal}$ m/s	u_{jj} m/s	u_{IDR} m/s
0.0	1138.6	1138.6	1138.6	1138.6	1138.6	1138.6
0.1	1144.6	1137.7	1176.1	1122.4	1162.9	1168.3
0.2	1160.9	1155.3	1210.9	1114.7	1188.5	1197.5
0.3	1174.3	1171.2	1242.3	1114.7	1214.4	1225.7
0.4	1208.9	1201.3	1270.7	1121.5	1240.5	1252.9
0.5	1242.9	1223.3	1296.6	1136.4	1266.7	1279.1
0.6	1248.1	1271.7	1320.1	1160.4	1293.0	1304.5
0.7	1271.1	1289.5	1341.7	1194.3	1319.3	1329.0
0.8	1292.0	1320.3	1361.6	1242.8	1345.6	1352.8
0.9	1329.2	1348.6	1380.0	1307.0	1371.8	1375.7
1.0	1398.3	1398.3	1398.3	1398.3	1398.3	1398.3

Table-II. Interaction parameter for collision factory theory, Nomato's empirical formula, Vandeel, Vangeel expression, Junjie method and Impedance dependence relation

mole fraction	CFT	VanDeel	Nomato	JJ	IDR
0.0	0	0	0	0	0
0.1	0.01198	0.03992	-0.05281	-0.03132	-0.04020
0.2	0.00959	0.08458	-0.08098	-0.04591	-0.06727
0.3	0.00531	0.11032	-0.10653	-0.06496	-0.08216
0.4	0.01135	0.16031	-0.09621	-0.05166	-0.07027
0.5	-0.03135	0.19453	-0.08232	-0.03856	-0.05714
0.6	-0.03677	0.15768	-0.10637	-0.06831	-0.08463
0.7	-0.02833	0.13257	-0.10269	-0.07183	-0.08537
0.8	-0.04248	0.08245	-0.09971	-0.07814	-0.08787
0.9	-0.02856	0.03419	-0.00723	-0.06122	-0.06655
1.0	0	0	0	0	0
Average interaction parameter	-0.12914	0.995971	-0.73469	-0.51191	-0.64146





The variation in theoretical values of ultrasonic velocities over whole concentration range is shown in figure-I. Similarly variation in percentage deviation is shown in figure-II. In table -II, the Nomato's relation shows the negative deviation over whole concentration and present in the range – 2.7013 to – 5.7687. According to VanDeel and Vangeel's ideal mixing relation the deviation is positive and present in the range 1.6701 to 8.5097. Junjies relation, Collision factor theory and Impedance dependence relation shows the deviation in the range – 1.5988 to – 4.1486, -2.1904 to +0.5940 and – 4.7058 to –2.0705 respectively. The Fig –II indicate that the percentage error is minimum for CFT hence it predicts the values of ultrasonic velocities close to experimental values for binary mixture containing α - picoline in ethanol. The theory proposes by Vandeel and vangeel's using ideal mixing relation shows the maximum deviation in theoretical values from experimental values.

Table-III. % deviation for ultrasonic velocity for collision factory theory, Nomato's empirical formula, Vandeel and Vangeel expression, Junjie method and Impedance dependence relation

mole fraction	u_{cft}	u_{Nomato}	$u_{Vandeeal}$	u_{jj}	u_{IDR}
0.0	0	0	0	0	0
0.1	0.5954	-2.752	1.9395	-1.5988	-2.0705
0.2	0.4737	-4.307	3.9795	-2.3774	-3.1527
0.3	0.2639	-5.7906	5.0753	-3.4148	-4.377
0.4	0.5638	-5.1816	7.1682	-2.6818	-3.7083
0.5	0.5696	-5.7687	8.5097	-1.9805	-2.9788
0.6	-1.8908	-5.5542	7.0507	-3.5974	-4.5188
0.7	-1.4475	-5.3869	6.042	-3.7919	-4.5551
0.8	-2.1904	-5.3869	3.808	-4.1486	-4.7058
0.9	-1.4535	-3.8218	1.6701	-3.2049	-3.4983
1.0	0	0	0	0	0
x^2	-4.5158	-43.9497	45.243	-26.7961	-33.5653
APE	-0.50176	-4.8833	5.027	-2.97734	-3.72948

CONCLUSION

In the present investigation CFT, Nomato's relation, VanDeel and Vangeel's ideal mixing relation, Jungie's relation and Impedance dependence relation are used for theoretical computation ultrasonic velocities in the binary liquid mixtures containing α–picoline in ethanol at 301.15K. From these theoretically calculated values of ultrasonic velocities it is conclude that the collision factory theory proposed by Shaft and Nutsch-Kuhnkies is found to best suited with experimental values having minimum percentage error over whole concentration range. Theoretical evaluation of ultrasonic velocity in this binary liquid mixtures and their comparison with experimental values reflects the existence molecular interaction.

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