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Experimental and theoretical investigations of ultrasonic speed in binary liquid mixtures of ascabin with isomers of butanol at T=313.15K

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ABSTRACT

Ultrasonic speed is measured at 2MHz frequency in the binary mixtures of ascabin with n-butanol/sec-butanol/tert-butanol and semi empirical values of acoustic speed have been evaluated at 313.15 K using Nomoto's relation, Vandeal's relation, Parsania's Impedance relation, Rao's and Junjie's method. Semi empirical values of acoustic speeds are compared with the experimental values and the validity of the theories is checked by calculating the percentage deviation. A good agreement has been found between experimental and Nomoto's ultrasonic speed.

KEY WORDS: Ultrasonic speed, density, semi empirical speed models.

1. INTRODUCTION

Measurement of acoustic speed gives the precious information about the physicochemical behaviour of the liquid and binary liquid mixtures. Ultrasonic speeds, densities and derived thermodynamic and acoustical parameters are of considerable interest in establishing molecular interactions in binary and ternary liquid mixtures. In the chemical industry knowledge of the thermodynamic properties of non-electrolyte solutions is essential in the design involving, heat shift, chemical partition, mass shift and fluid flow. Acoustic studies can also be used to find out the degree of complexation and to calculate the formation constant values of charge shift complex. Measurement of ultrasonic speed has been sufficiently employed in establishing the type of molecular interaction in pure liquid and liquid mixtures. The useful application of mixed solvents rather than single solvent in industrial and biological process has been accepted all around the world as they give a wide choice of solutions with relevant properties.

The present study deals with the thermodynamic study of mixed liquid system at 313.15 K temperature. The liquids under exploration have been chosen on the basis of wide applications and industrial importance. These applications have intensely stimulated the need for broad and depth information on the thermodynamic, acoustic, transport properties of these solvents and their mixtures.

Ascabin is a carboxylate ester, which is used as pest repellent, drug for skin related diseases and oily injection. Behaviour of ascabin in various liquids such as aliphatic alkanes, aromatic alkenes, aliphatic alcohols, substituted benzenes, acetates, ketones and DMSO (super solvent) has been systematically studied acoustically.

We know that alkanols are self- connected organic liquids, used for the production of several organic compounds. They are also widely used as coupling and dispersing agent in the pharmaceutical, chemical and domestic industry and as a transporter and extraction of solvents for natural products. Branching of CH3 group attached to the -OH group results in anomalous behaviour of alcohols. The action of alkanol [s] with organic liquids is remarkable due to its acidic property. The O-H bonds in alkanols are polar and allow the liberation of the H atom as proton (H+). The order of acidity in alcohols is: 1°-alcohol> 2°- alcohol > 3°-alcohol. This order is due to +I effect.

As an extension of our earlier work, we report here the acoustic speed evaluated using Nomoto's relation, Impedance relation, Ideal mixture relation and Junjie's method for the binary mixtures of Ascabin with n-butanol/sec-butanol/tert-butanol. Moreover, the best suitable theory for the given molecular system under study is also picked out by deriving the percentage deviation.

2. EXPERIMENTAL DETAILS

High purity Analytical Reagent (AR) grade samples of Ascabin (BB) (sd fine chemicals), n-butanol (Fluka), sec-butanol procured from Merck and tert-butanol procured from Sigma Aldrich were used. Before the experiment, all the chemicals were cautiously dried over 0.4 nm molecular sieves and stored in dark bottles. These chemicals were further purified by standard methods.

The solutions of binary mixtures BB with alkanols have been prepared in the specially designed glass bottles with air tight stoppers and suitable measures have been taken to minimize evaporation losses. All the binary liquids were carefully dried over 0.4 nm molecular sieves further and stored in clear dark bottles well before the measurements. These binaries were distilled just before use.

The purity of these binaries was measured by Gas Chromatography (HP 8610) using a FID detector and the analysis indicated mole percent purities > 99.5 %. The weighing of binaries has been made with a METTLER TOLEDO (Switzerland make) ABB5-S/FACT digital balance with an accuracy of ±10-2 mg. The uncertainty in the mole fraction is 10-4.

The acoustic speed (u) of pure liquids and binaries have been measured using an acoustic interferometer (Mittal type, Model M-82) working at 2 MHz fixed frequency with an accuracy of±0.01ms-1. Densities (ρ) of pure liquids and their binary mixtures have been evaluated with a 10 cm3 two stem double-walled Parker & Parker type pycnometer. The procedure for measuring u and ρ has been described in our earlier papers. The repeatabilities in the measured parameter of density is 3 in 0.0001 parts and in mole fraction is ±0.0002.

3. RESULTS AND DISCUSSION

The experimentally measured values of ultrasonic speed (u) and density (ρ) at313.15 K of all pure liquids have been compared with the literature values in Table 1.

Table.1.Comparison of experimental values of density (ρ) and speed (u) of pure liquids with the corresponding literature values at 313.15 K

Pure Liquid	T/(K)	ρ/(kgm^{-3})		u/(ms^{-1})	
		Expt.	Litt.	Expt.	Litt.
Ascabin	313.15	1109.77	1109.7	1471.44	1471.4
n-butanol	313.15	792.30	792.3	1181.50	1181.5
sec-butanol	313.15	791.10	791.1	1159.10	1159.1
tert-butanol	313.15	766.91	766.9	1065.61	1065.6

In the present study, semi empirical sound speeds have been evaluated by considering BB as one component and *n*-butanol/*sec*-butanol/*tert*-butanol as the other component in the binaries at T=313.15K. Such an evaluation of semi empirical sound velocity is useful to verify the applicability of various postulates of the theories of liquid mixtures and to arrive at some useful inferences on the subject of the (strength of) molecular interactions between component liquids in some cases. Theoretically evaluated various semi empirical ultrasonic speeds have been presented in Tables 2-4 at 313.15 K for BB+*n*-butanol/BB+*sec*-butanol/BB+*tert*-butanol respectively using the following standard equations and standard errors of these empirical values are tabulated in Table 5.

Nomoto established the following semi empirical equation for sound speed based on the assumption of the linearity of the molecular sound speed and the additivity of molar volume.

$$U_N = \{(\Sigma x_i R_i)/(\Sigma x_i V_i)\}^3, \quad (1)$$

The Impedance Dependence Relation is given below

$$U_{imp} = \Sigma x_i Z_i / \Sigma x_i \rho_i, \quad (2)$$

Van Dael obtained the Ideal Mixture Relation

$$\Sigma(x_i M_i / u_i^2) = \{1/\Sigma x_i M_i\}\{1/U_V\}^2, \quad (3)$$

Specific sound speed relation is given by

$$U_R = (\Sigma x_i r_i \rho)^3, \quad (4)$$

Where $r_i = \frac{(u_i)^{\frac{1}{3}}}{\rho_i}$ is Rao's specific sound speed of i^{th} component of the mixture.

Junjie's equation is given by

$$U_{Jun} = \{\Sigma x_i V_i / (\Sigma x_i M_i)^{1/2}\}\{\Sigma(x_i V_i / \rho_i u_i^2)\}^{-1/2}, \quad (5)$$

Where x_i is mole fraction, M_i is molecular weight, R_i is the molar sound speed, Z_i is acoustic impedance, ρ_i is density, V_i is the molar volume, u_i is the speed of sound of the i th component and U_V is the Van Dael's velocity. Percentage deviation in acoustic speed is given by

$$\% \Delta u = 100 * [1 - \frac{U_{cal}}{u_{\exp}}] \quad (6)$$

Table.2.Densities (ρ), experimental ultrasonic speed (U_{expt}) and empirical ultrasonic speed equations for the system (BB+*n*-butanol) as a function of mole fraction (x_1) of ascabin at T=313.15 K

x_1	P /(kgm^{-3})	Uexpt.	U_N	U_V /	U_I	U_R	U_J
1.0000	1109.77	1471.44	1471.44	1471.44	1471.48	1471.44	1471.44
0.9234	1091.35	1454.95	1459.33	1342.89	1455.26	1498.72	1447.01
0.8854	1082.94	1449.67	1452.98	1295.34	1446.94	1514.15	1434.89
0.7631	1066.08	1426.74	1430.77	1187.50	1418.84	1604.76	1395.98

0.6688	1046.11	1409.67	1411.55	1135.73	1395.70	1640.35	1366.14
0.5914	1028.88	1396.44	1394.18	1107.16	1375.65	1662.21	1341.83
0.4753	1000.28	1370.59	1364.93	1082.52	1343.61	1674.88	1305.90
0.3270	951.57	1326.66	1320.69	1077.84	1298.85	1615.65	1261.62
0.2768	931.40	1309.36	1303.57	1082.76	1282.62	1573.05	1247.28
0.1400	870.88	1256.40	1249.95	1114.37	1235.24	1421.15	1211.04
0.0000	792.30	1181.50	1181.50	1181.50	1181.37	1181.50	1181.50

Table.3.Densities (ρ), experimental ultrasonic speed (U_{expt}) and empirical ultrasonic speed equations for the system (BB+*sec*-butanol) as a function of mole fraction (x_1) of ascabin at T=313.15 K.

x_1	ρ/(kgm^{-3})	Uexpt.	U_N	U_V/ (ms^{-1})	U_I	U_R	U_J
1.0000	1109.77	1471.44	1471.44	1471.44	1471.48	1471.44	1471.44
0.9243	1092.72	1455.92	1458.46	1337.19	1454.25	1501.07	1444.94
0.8868	1085.29	1448.46	1451.67	1287.88	1445.43	1519.01	1431.86
0.7361	1063.37	1421.19	1421.59	1156.67	1407.90	1621.64	1379.72
0.6787	1052.07	1411.25	1408.82	1125.42	1392.67	1645.81	1360.08
0.5906	1032.93	1394.00	1387.53	1090.96	1368.18	1671.40	1330.25
0.4689	997.51	1361.68	1354.26	1064.53	1331.95	1654.89	1289.88
0.3293	950.79	1317.46	1309.24	1059.25	1286.53	1591.94	1245.40
0.2797	931.65	1299.78	1291.09	1063.47	1269.28	1553.38	1230.29
0.1404	866.92	1243.00	1232.57	1093.84	1217.37	1383.40	1190.94
0.0000	791.10	1159.10	1159.10	1159.10	1159.15	1159.10	1159.10

Table.4.Densities (ρ), experimental ultrasonic speed (U_{expt}) and empirical ultrasonic speed equations for the system (BB+*tert*-butanol) as a function of mole fraction (x_1) of ascabin at T=313.15 K

x_1	ρ/(kgm^{-3})	Uexpt.	U_N	U_V/ (ms^{-1})	U_I	U_R	U_J
1.0000	1109.77	1471.44	1471.44	1471.44	1471.48	1471.44	1471.44
0.9231	1095.99	1450.64	1453.33	1302.74	1449.37	1517.51	1430.74
0.8896	1090.05	1442.35	1445.03	1250.24	1439.40	1537.33	1413.48
0.7356	1061.68	1402.42	1403.31	1095.46	1390.67	1619.26	1337.62
0.6815	1050.65	1391.57	1387.09	1062.25	1372.33	1641.07	1312.30
0.5997	1032.33	1370.27	1360.78	1025.27	1343.27	1663.52	1275.31
0.4619	994.73	1322.66	1310.84	989.95	1290.34	1658.98	1216.61
0.3312	947.12	1265.53	1255.57	981.10	1234.88	1581.75	1165.52
0.2795	927.14	1239.90	1231.16	983.63	1211.35	1541.91	1146.72
0.1433	858.96	1167.22	1158.46	1007.47	1144.48	1353.75	1102.02
0.0000	766.90	1065.60	1065.60	1065.60	1065.33	1065.60	1065.60

It can be seen from Table 2-4 that the theoretical values of acoustic speed computed by various theories illustrate variation from experimental values. The predictive abilities of several acoustic empirical equations depend upon the strength of interaction prevailing in a system. These relations generally fail to establish accurately the acoustic speeds where strong interactions are supposed to exist. Figures 1-3 are drawn by taking mole fraction (x_1) on X-axis and percentage deviation (%ΔU) on Y-axis at 313.15 K for BB+*n*-butanol, BB+*sec*-butanol and BB+*tert*-butanol respectively. It is clear from the Figures 1-3 that, among all the empirical theories, Nomoto's semi empirical equation gives the best estimate of experimental values of sound speed in all the systems followed by Parsania's impedance semi empirical equation.

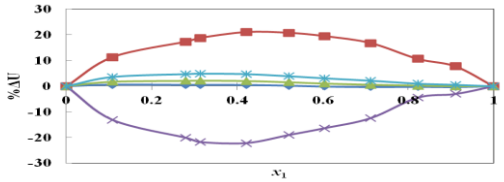

Fig.1.Plots of percentage deviations of theoretical ultrasonic speeds (%ΔU) of (BB +*n*-butanol) binary system with mole fraction (x_1) of BB, Nomoto (♦), Van Dael (■), Impedance (▲), Rao's(x), and Junjie (x) at T=313.15K

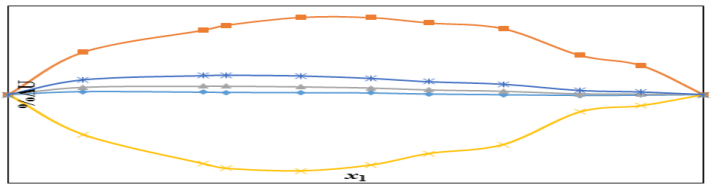

Fig.2.Plots of percentage deviations of theoretical ultrasonic speeds (%ΔU) of (BB +*sec*-butanol) binary system with mole fraction (x_1) of BB, Nomoto (♦), Van Dael (■), Impedance (▲), Rao's(x), and Junjie (x) at T=313.15K

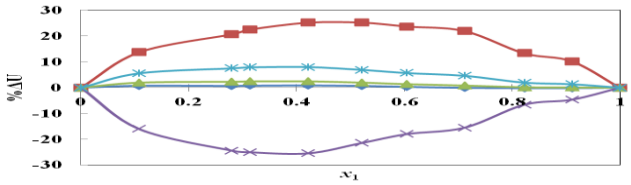

Fig.3.Plots of percentage deviations of theoretical ultrasonic speeds (%ΔU) of (BB +*tert*-butanol) binary system with mole fraction (x_1) of BB, Nomoto (♦), Van Dael (■), Impedance (▲), Rao's(x), and Junjie (x) at T=313.15K

An important reason for variation from experimental values of acoustic speed is that the molecular association effects are not taken into account in these theories. When two liquids are mixed, the interaction between the molecules of the two liquids takes place because of the existence of several forces like dispersive force, charge transfer, hydrogen bonding, dipole-dipole and dipole-induced dipole interactions. Hence the observed variation shows that the molecular interaction is taking place between the unlike molecules in the liquid mixture.

In the present binaries, the difference between experimental and theoretical speeds is larger where the mole fraction of BB varies in the region 0.4 to 0.6. Hence it can be qualitatively inferred that the strength of molecular interaction in the binaries is greater in this range of mole fraction of binary mixtures. Further, higher deviations suggest the existence of strong affinity for the association between component molecules as a result of Hydrogen bonding in the present systems.

4. CONCLUSION

- Densities, ultrasonic speeds for binary liquids of BB with *n*-butanol/*sec*-butanol/*tert*-butanol have been measured experimentally over the mole fraction range at T=313.15 K.
- The acoustic speeds evaluated from various speed theories have been correlated with the experimentally measured acoustic speeds and their percentage deviations have been evaluated. Among all the empirical theories Nomoto's relation is found to give the best estimate of experimental values of sound speed in all the systems investigated.

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