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Theoretical Evaluation and Experimental Study of Ultrasonic Velocities in Binary Liquid Mixtures of Trichloroethylene with Three Alcohols At 303.15 K

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Abstract : Theoretical velocities of binary liquid mixtures of Trichloroethylene (TE) with 1-Pentanol, 1-Hexanol, and 1-Heptanol at T = (303.15) K have been evaluated by employing two theoretical models of the ultrasonic velocity determination, viz. Nomoto (NOM) and Van Dael & Vangeel (VDV). Ultrasonic velocities and densities of these mixtures have also been measured experimentally as a function of composition. A good agreement is found between experimental and theoretical values. U^2_{exp}/U^2_{imx} has also been evaluated for non-ideality in the mixtures. The results are discussed in terms of intermolecular interactions between the component molecules in these binary liquid mixtures.

Keywords : Theoretical ultrasonic velocities, experimental velocities, Hydrogen bonding, molecular interaction parameter.

Introduction:

Extensive studies are carried out in the field of ultrasonic measurements in organic liquids mixtures [1-10] to assess different types of molecular interactions. The various physical and chemical properties such as molar volume and adiabatic compressibility are obtained from ultrasonic velocity and density. Ultrasonic velocities in binary liquids are calculated and compared with the experimental values [11-21]. This study is in continuation of a research programme undertaken for comparison of experimental ultrasonic velocity with the theoretically estimated values obtained by employing models of Nomoto and Van Deal ideal mixing relations, for the binary mixtures of various systems at 303.15K. Nomoto relation holds good for the binary mixture at the temperature of the present study. The intermolecular interactions between these binary liquid mixtures are evaluated using these results [22-30]. The paper reports the comparison between the experimental and theoretical ultrasonic velocities of the binary liquid mixtures of Trichloroethylene with 1-Pentanol, 1-Hexanol and 1-Hepatanol at 303.15K over the entire composition range, evaluated by using two theories viz., Nomoto (NOM) and Van Dael and Vangeel (VDV) relations. [31-40].

Experimental Section

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

The density (ρ) of pure liquids and their mixtures is determined using a $10^{-5}m^3$ double - arm pycnometer, at temperature $303.18^{o}k$ are reproducible within 2 x 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 ±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) and regulated to ±0.01 K, using a proportional temperature controller. Adequate precautions were taken to minimize evaporation losses during the actual measurements. The ultrasonic velocity (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 ± 0.1 m. sec^{-1}. The temperature stability was maintained within ± 0.01K.by circulating water bath around the measuring cell through a pump.

Theoretical considerations

Nomoto Equation

Rao found experimentally that, for pure liquids, the ratio of temperature coefficients of sound velocity U and molar volume V remains almost constant:

$$[(1/U)(dU/dT)] / [(1/V)(dV/dT)] = -3 \qquad (1)$$

Where T is the absolute temperature. Integrating equation (1) obtains:

$$Vu1/3. = R = (M/\rho)\, u1/3 = R \qquad (2)$$

Where M is the molecular weight and ρ is density. The constant R is called the molar sound velocity or Rao's constant. It was found to be additive. It can be calculated as a sum of increments from the atoms or atom groups in the molecule from the chemical bonds

On assuming the additivity of molar sound velocity (R) and no volume change on mixing, Nomoto established the following relation6 for a liquid mixture

$$R = (M/\rho)\, U1/3 \qquad (3)$$

Where U and ρ are determined experimentally and M is the mean molecular weight in a binary liquid mixture

$$M = (X_1M_1 + X_2M_2) \qquad (4)$$

Where M_1 and M_2 are molecular weights of constituent components.

Simple manipulation yields the following relation,

$$U_{Nomoto} = [(X_1R_1+X_2R_2) / (X_1V_1+X_2V_2)]^{3} \qquad (5)$$

The Van Deal and Vangeel Equation and Waddington66, yield the following relation for adiabatic compressibility $(\beta ad)_{imx}$ The ideal mixing theory advanced by Van Dael and Vangeel in the light of assumptions made by Blandamer,

$(\beta ad)imx = \phi 1\gamma 1/\gamma imx\ (\beta ad)1 + \phi 2\ \gamma 2/\gamma imx\ (\beta ad)2$. (6)

Where, ϕ_1, ϕ_2 are the volume fraction of species 1 and 2, γ_1 and γ_2 are ratios of specific heats of the respective species. This relation holds good if the mixture is ideal and if $\gamma 1 = \gamma 2 = \gamma max$. Using the additional assumption that $V_1 = V_2$ the above equation can be transformed into a linear combination of mole fraction X_1 and X_2.

$(\beta ad)\ imx = X_1\ (\beta ad)_1 + x\ X_{12}(\beta ad)_2$ ……………… .(7)

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

$1/(X_1M_1+X_2+M_2)*1/U^2_{imx} = X_1/M_1U_1^2 + X_2/M_2U_2^2$ (8)

Where Umix is the ideal mixing ultrasonic velocity in liquid mixture.U_1 and U_2 are ultrasonic velocities in species.

Results and Discussion

Binary liquid mixtures studied in this paper are

1. **Trichloroethylene + 1-Pentanol**
2. **Trichloroethylene + 1-Hexanol**
3. **Trichloroethylene + 1-Heptanol**

The experimental values along with the values calculated theoretically using the relations of Nomoto and Van Deal ideal mixing for trichloroethylene + 1-pentanol, trichloroethylene + 1-hexanol and trichloroethylene + 1-heptanol at the temperature of 303.15 are given in Tables 1-3. The validity of different theoretical formulae is checked by percentage deviation for all the mixtures and is also given in Tables 1-3 and their respective graphs are shown in the Figs 1-3.

It can be seen from Tables 1-3, that the theoretical values of ultrasonic velocity computed by various theories show deviations from experimental values. The limitations and approximations incorporated in these theories are responsible for it. It is assumed that all the molecules are spherical in shape, which is not true. In Nomoto's theory, it is assumed that the volume does not change on mixing. Therefore, no interaction between the components of liquid mixtures has been taken into account. The assumption for the formation of ideal mixing relation is that, the ratio of specific heats of ideal mixtures and the volumes are also equal. Again, no molecular interaction is taken into account. Similarly, the assumption for the Collision Factor theory, the molecules is treated as real non-elastic substances in this theory, which is not really the case.

But on mixing two liquids, the interaction between the molecules of the two liquids takes place because of 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 interaction is taking place between the unlike molecules in the liquid mixture.

Fig. 1-3 represent the variation of U^2_{exp} / U^2_{imx} with mole fraction of trichloroethylene. A maximum is observed in trichloroethylene + 1-pentanol system at approximately 0.55 and it is maximum in the case of trichloroethylene+ 1-hexanol and trichloroethylene + 1-heptanol systems at approximately 0.58 and 0.52 respectively.

The validity of various theoretical approaches of liquids has been tested for the binary systems of trichloroethylene + 1-pentanol, trichloroethylene + 1-hexanol and trichloroethylene + 1-heptanol by comparing theoretical sound speeds with those experimentally determined at the temperature of 303.15K. The experimental values of sound speed for the three systems along with theoretical values and percentage deviations for Nomoto's Relation (NOM) and Van deal and Vangeel Ideal Mixing relation are compared for the three binaries. In the three systems Nomoto's Relation exhibits more satisfactory agreement with the experimental values at the temperature studied (303.15K).

The percentage deviations of the ultrasonic velocity are both negative and positive. Such deviations indicate the non-ideal behavior of liquid mixtures. The ratio U^2_{exp} / U^2_{imx} is used as an important tool to measure the non-ideality in the mixtures, especially in these cases where the properties other than sound velocity are not known. A perusal of Tables 1-3 indicate considerable deviations from ideality, which may be due to the existence of strong tendency for the formation of association in liquid mixtures through dipole-dipole interactions.

It is observed that for binary mixtures of trichloroethylene + 1-pentanol, trichloroethylene + 1-hexanol and trichloroethylene + 1-heptanol, the minimum percentage of deviation is exhibited by Nomoto relation and followed by Van Deal's relation. This is in good agreement with the conclusions drawn by others.

Nomoto's relation is based on additivity of molar sound velocity and isochoric condition under which volume remains unchanged even after mixing of the components. But large positive deviations of experimental values from the theoretical values computed using Nomoto's relation imply that molar sound velocity is not additive and volume of the system does not remain constant. This implies that chemical forces such as hydrogen bonding and dipole-dipole interactions between unlike molecules are present in the system. This is attributed to be the consequence of that intermolecular free length in the liquid mixtures is less than the ideal free length. This indicates that the component molecules in the liquid mixture have a more compact arrangement than in component liquids forming the mixture.

Table-1 System-1 Trichloroethylene + pentanol

Temperature – 303.15K

Mole fraction X	**U_{exp} m/s**	**U_{Nomoto} m/s**	**U_{imx} m/s**	**% U_{No}**	**% U_{imx}**	**U^2_{exp}/U^2_{imx}**
0.0000	1264.50	1264.50	1264.50	0.0000	0.0000	1.0000
0.1183	1235.20	1238.01	1226.48	0.2272	-0.7056	1.0143
0.2319	1206.06	1211.88	1192.77	0.4826	-1.1024	1.0224
0.3411	1178.31	1186.13	1162.63	0.6640	-1.3308	1.0272
0.4460	1152.00	1160.74	1135.50	0.7591	-1.4325	1.0293
0.5471	1127.35	1135.72	1110.93	0.7429	-1.4560	1.0298
0.6443	1104.00	1111.07	1088.58	0.6400	-1.3971	1.0285
0.7381	1082.28	1086.77	1068.13	0.4145	-1.3077	1.0267
0.8285	1061.74	1062.82	1049.34	0.1023	-1.1673	1.0238
0.9158	1041.09	1039.24	1032.03	-0.1781	-0.8707	1.0176
1.0000	1016.00	1016.00	1016.00	0.0000	0.0000	1.0000

Table-2 System -2 Trichloroethylene + hexanol

Temperature – 303.15K

Mole fraction X	**U_{exp}** m/s	**U_{Nomoto}** m/s	**U_{imx}** m/s	**% U_{No}**	**% U_{imx}**	**U^2_{exp}/U^2_{imx}**
0.0000	1275.50	1275.50	1275.50	0.0000	0.0000	1.0000
0.1342	1248.31	1247.76	1233.18	-0.0438	-1.2118	1.0247
0.2586	1219.40	1220.43	1196.41	0.0849	-1.8849	1.0388
0.3741	1190.40	1193.50	1164.16	0.2603	-2.2045	1.0456
0.4818	1163.12	1166.97	1135.65	0.3311	-2.3622	1.0490
0.5824	1137.27	1140.84	1110.25	0.3132	-2.3763	1.0493
0.6766	1112.52	1115.10	1087.49	0.2315	-2.2499	1.0466
0.7650	1089.06	1089.74	1066.97	0.0628	-2.0280	1.0418
0.8480	1066.64	1064.78	1048.39	-0.1748	-1.7117	1.0351
0.9262	1044.25	1040.20	1031.47	-0.3878	-1.2242	1.0249
1.0000	1016.00	1016.00	1016.00	0.0000	0.0000	1.0000

Table-3 System -3 Trichloroethylene + Heptanol

Temperature – 303.15K

Mole fraction X	**U_{exp}** m/s	**U $_{Nomoto}$** m/s	**U_{imx}** m/s	**% U_{No}**	**% U_{imx}**	**U^2_{exp}/U^2_{imx}**
0.0000	1316.00	1316.00	1316.00	0.0000	0.0000	1.0000
0.1503	1286.74	1283.65	1258.32	-0.2399	-2.2088	1.0457
0.2847	1253.53	1251.83	1211.44	-0.1353	-3.3574	1.0707
0.4056	1220.44	1220.54	1172.56	0.0082	-3.9233	1.0833
0.5149	1188.66	1189.78	1139.77	0.0947	-4.1130	1.0876
0.6142	1158.64	1159.54	1111.72	0.0780	-4.0497	1.0862
0.7048	1129.77	1129.82	1087.44	0.0041	-3.7468	1.0794
0.7879	1101.67	1100.61	1066.22	-0.0969	-3.2182	1.0676
0.8643	1074.68	1071.90	1047.51	-0.2582	-2.5283	1.0526
0.9348	1048.29	1043.70	1030.88	-0.4378	-1.6613	1.0341
1.0000	1016.00	1016.00	1016.00	0.0000	0.0000	1.0000

Graphs

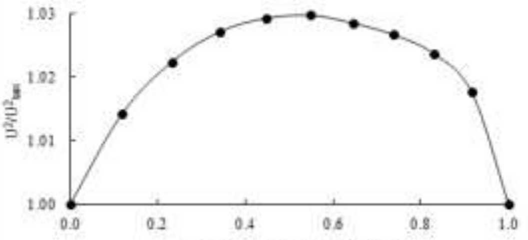

Fig 1 Variation of U^2/U^2_{imx} with molefraction of trichloroethylene for trichloroethylene +1-pentanol system

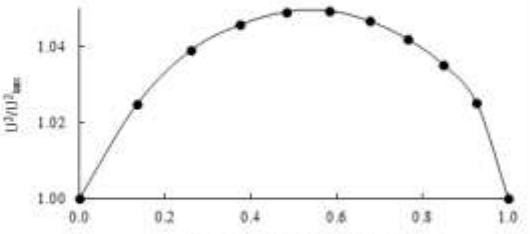

Fig 2 Variation of U^2/U^2_{imx} with molefraction of trichloroethylene for trichloroethylene + 1-hexanol system

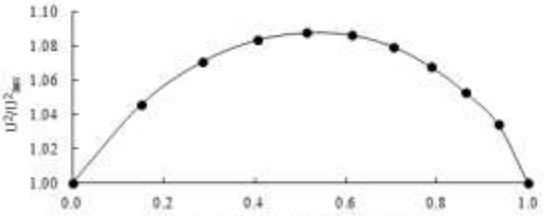

Fig 3 Variation of U^2/U^2_{imx} with molefraction of trichloroethylene for trichloroethylene + 1-heptanol system

Conclusions

It is concluded that out of the two theories and relations discussed above, the Nomoto's relations, provide the best results. Thus, the linearity of molar sound velocity and additivity of molar volumes as suggested by Nomoto and Van Deal and Vangeel in deriving the empirical relations (5) and (8) are these have been truly observed in the aforementioned binary liquid mixtures. The success of Nomoto's relation in predicting the experimental ultrasonics velocities for the polar-polar liquid mixtures has also been emphasized by others.

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