Volume : 3 | Issue : 11 | November 2014 • ISSN No 2277 - 8179

Research Paper

Theoretical Evaluation of Ultrasonic Velocities in Ternary Liquid Mixture of Tetrahydrofuran+Hexane+Decane at Different Temperatures

Physics

KEYWORDS : Ultrasonic velocity, Collision factor theory, Ideal mixing relation and Average Percentage Error.

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ABSTRACT

Ultrasonic velocities and densities of the ternary liquid mixtures of tetrahydrofuran+hexane+decane have been measured at temperatures 303 K, 308 K and 313 K over the entire composition range of mole fractions. The theoretical values of ultrasonic velocity were evaluated using Nomoto's Relation (UNR),Junjie's Method (UJM), Ideal Mixing Relation (UIMR), Free Length Theory (UFLT), Collision Factor Theory (UCFT) and Impedance Dependence Relation (UIDR). Theoretical values are compared with the experimental values and the validity of the theories is checked by calculating the average percentage error (APE).

Introduction:

In recent years measurement of ultrasonic investigations found extensive applications in determining the physicochemical behaviour of liquid mixture. Theoretical evaluations of ultrasonic velocity give a better understanding of molecular arrangements in liquids. Several researchers [1,2]carried out ultrasonic investigation and correlated the experimental results of ultrasonic velocity with the theoretical relation of Nomoto, Junjie's relation ,Van Deal and Vangeel Ideal mixing relation , Free length theory , Collision factor theory, Impedance dependence relation and interpreted the results in terms of molecular interactions. The aim of the present work is to compare the merits of both the methods and to investigate the degree of molecular interactions in the ternary mixtures.

Experimental Techniques:

All the chemical used are of analytical reagent (AR) and spectroscopic reagent (SR) without further purification. The purities of the above chemicals were checked by density determination at 303, 308 and 313 ± 0.1 K, which showed an accuracy of $\pm 1\times10^{-4}$ gcm^{-3}. The ternary liquid mixtures of different known compositions were prepared in stopper measuring flasks. The density and velocity were measured as a function of composition of the ternary liquid mixture at 303, 308 and 313K for mixed solvent systems in which tetrahydrofuran wasadded to a binary mixtures of hexane and decane. For this purpose binaries with fixed volume ratios ≅ 3:1were prepared. The density was determined using a specific gravity bottle by relative measurement method with an accuracy of ± 0.01 kgm^{-3}. The weight of the sample was measured using electronic digital balance with an accuracy of ± 0.1 mg (Model: SHIMADZU AX-200). An ultrasonic interferometer having the frequency of 3 MHz (MITTAL ENTERPRISES, New Delhi, Model: F-81) with an overall accuracy of ± 0.1% has been used for velocity measurement. An electronically digital operated constant temperature bath (RAAGA Industries) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature. The accuracy in the temperature measurement is ± 0.1 K.

Theory and Calculations:

Nomoto's Relations (NR)[3]

$$U_{NOM} = \left[\frac{X_1R_1+X_2R_2+X_3R_3}{X_1V_1+X_2V_2+X_3V_3}\right]^3$$

Where, Molar sound velocity,

$$R_1 = \frac{m_1}{d_1}U_1^{1/3} \; ; R_1 = \frac{m_2}{d_2}U_2^{1/3} \; ; R_3 = \frac{m_3}{d_3}U_3^{1/3}$$

$$\text{Molar volume } V_1 = \frac{m_1}{d_1} ; V_2 = \frac{m_2}{d_2} ; V_3 = \frac{m_3}{d_3}$$

Junjie'sMethod (JM)4

$$U_{JM} = \left[\frac{X_1V_1+X_2V_2+X_3V_3}{X_1m_1+X_2m_2+X_3m_3}\right]^{1/2}\left[\frac{X_1V_1}{d_1U_1^2}+\frac{X_2V_2}{d_2U_2^2}+\frac{X_3V_3}{d_3U_3^2}\right]^{-1/2}$$

Ideal Mixing Relation (IMR)5

$$U_{IMR} = \left[\frac{1}{X_1m_1+X_2m_2+X_3m_3}\right]^{1/2}\left[\frac{X_1}{m_1U_1^2}+\frac{X_2}{m_2U_2^2}+\frac{X_3}{m_3U_3^2}\right]^{-1/2}$$

The degree of molecular interaction (α)6 is given by

$$\alpha = \frac{U_{exp}^2}{U_{IMR}^2} - 1$$

Free Length Theory (FLT)7

$$= \frac{K}{L_{f_{mix}}\, d_{exp}^{1/2}}$$

$$\text{Where,} \quad L_{f_{mix}} = 2\left[\frac{V_m-(X_1V_{01}+X_2V_{02}+X_3V_{03}}{X_1Y_1+X_2Y_2+X_3Y_3}\right]$$

Molar volume at absolute zero, $V_{01} = V_1 \frac{U_1}{U_\propto}$;

$V_{02} = V_2 \frac{U_2}{U_\propto}$; $V_{03} = V_3 \frac{U_3}{U_\propto}$

Surface area per mole, $Y_1 = \frac{2(V_1 - V_{01})}{L_{f1}}$; $Y_2 = \frac{2(V_2 - V_{02})}{L_{f2}}$; $Y_3 = \frac{2(V_3 - V_{03})}{L_{f3}}$

Where, 1, 2, represents the first and second component of the liquid mixture and the other symbols have their usual meanings.

Impedance Dependence Relation (IDR)8

$$U_{IDR} = \frac{X_1 Z_1 + X_2 Z_2 + X_3 Z_3}{X_1 \rho_1 + X_2 \rho_2 + X_3 \rho_3}$$

Collision Factor Theory (CFT)9

$$U_{CFT} = \frac{U_\infty \sum x_i S_i \sum x_i B_i}{V_{mix}}$$

Here, U_∞ = 1600 ms^{-1} , S is the collision factor and B the actual volume of molecule per mole, given as,

$$B = \frac{4\pi}{3} r_m^3 \text{ N}$$

where r_m stands for molecular radius and N the Avogadro number. The value of r_m has been obtained using Schaaffs expression as follows

$$r_m = \left(\frac{3b}{16\pi N}\right)^{1/3}$$

$$b = \left(\frac{m}{\rho}\right)\left[1 - \frac{RT}{mu^2}\left\{\sqrt{1 + \frac{mU^2}{3RT}} - 1\right\}\right]$$

Average Percentage Error (APE)10

$$\text{APE} = \frac{1}{n}\sum_{i=1}^{n} \frac{U_{exp} - U_{theo}}{U_{exp}} \times 100$$

Average Percentage Error (APE)[10]

APE = 100

Where, n- number of data used.

U_{exp} = experimental values of ultrasonic velocities of mixtures.

U_{theo} = theoretically computed values of ultrasonic velocities of mixtures.

In all the above equations the symbols used have their usual meanings.

Results and Discussion:

The values of ultrasonic velocities computed theoretically using the relations of Nomoto, Junjie, Van Dael and Vangeel, Jacobson's Free Length Theory, Impedance Dependence Relation and Schaaf's Collision Factor Theory together with experimental values for the ternary mixture of tetrahydrofuran(x_1)+hexane(x_2)+decane(x_3) at the temperatures 303 K, 308 K and 313 K are summarised in Table 1. The percentage deviation and Average Percentage Error (APE) of sound velocity using the above theory and molecular interaction term α for the mixtures studied are given in Table 2.

A general survey of Table-2 shows that α is positive. The positive values of α in the system at all the temperatures clearly indicate the existence of strong tendency for the

Table-1: Experimental and theoretical values of velocities in tetrahydrofuran(x_1)+hexane(x_2)+decane(x_3) (x_2/x_3=3:1) at 303, 308 and 313 K.

Mole Fraction X_1	U_{EXP} ms^{-1}	U_{NR} ms^{-1}	U_{JM} ms^{-1}	U_{IMR} ms^{-1}	U_{FLT} ms^{-1}	U_{CFT} ms^{-1}	U_{IDR} ms^{-1}
303K							
0.0	1136.0	1101.3	1093.0	1051.7	1097.6	1093.5	1093.9
0.1	1176.3	1109.4	1096.4	1067.7	1090.2	1096.7	1114.1
0.2	1159.1	1118.5	1100.8	1084.3	1120.7	1122.4	1133.0
0.3	1154.8	1128.5	1106.3	1101.7	1072.0	1118.9	1150.7
0.4	1143.2	1139.7	1113.5	1119.9	1056.5	1127.0	1167.4
0.5	1130.0	1152.4	1122.8	1139.0	1025.3	1128.5	1183.2
308K							
0.0	1099.2	1058.7	1049.8	1008.8	1081.1	1060.9	1051.2
0.1	1135.7	1066.3	1052.7	1024.0	1055.7	1064.1	1070.3
0.2	1120.0	1074.7	1056.5	1039.9	1077.3	1085.4	1088.2
0.3	1118.7	1084.0	1061.5	1056.5	1028.6	1078.3	1104.9
0.4	1105.4	1094.4	1068.0	1073.8	1029.8	1090.8	1120.6
0.5	1098.6	1106.2	1076.5	1092.0	1001.0	1090.1	1135.4
313K							
0.0	1047.0	1026.3	1018.9	981.3	1068.8	1038.0	1020.0
0.1	1075.8	1033.0	1021.2	994.8	1055.3	1044.0	1037.1
0.2	1063.8	1040.5	1024.2	1008.9	1043.7	1050.4	1053.1
0.3	1057.2	1048.8	1028.3	1023.7	1022.2	1052.0	1068.1
0.4	1051.8	1058.0	1033.7	1039.2	992.9	1049.3	1082.1
0.5	1039.2	1068.5	1041.1	1055.4	972.9	1050.0	1095.2

Table-2: Percentage deviation , Average Percentage Error and molecular interaction parameter values for the system tetrahydrofuran (x_1)+hexane(x_2)+decane(x_3) (x_2/x_3=3:1) at 303, 308 and 313 K.

Mole Fraction X_1	% U_{NR}	% U_{JM}	% U_{IMR}	% U_{FLT}	% U_{CFT}	% U_{IDR}	α
303K							
0.0	3.0587	3.78163	7.41849	3.38106	3.74427	3.70287	0.1667
0.1	5.6857	6.78944	9.23469	7.32276	6.76489	5.28951	0.2138
0.2	3.5070	5.03194	6.45214	3.30878	3.16453	2.25436	0.1427
0.3	2.2783	4.19698	4.59809	7.17087	3.11018	0.35335	0.0987
0.4	0.3047	2.59873	2.03862	7.58442	1.41773	-2.11943	0.0421
0.5	-1.9783	0.63851	-0.79274	9.26465	0.13233	-4.70689	-0.0157
APE	2.14267	3.83954	4.82488	6.33876	3.05566	0.79563	-
308K							
0.0	3.68438	4.49436	8.22044	1.64900	3.48355	4.36700	0.1872
0.1	6.11325	7.30626	9.83234	7.04249	6.30419	5.75891	0.2300
0.2	4.04889	5.66656	7.15267	3.81516	3.08605	2.84301	0.1600
0.3	3.10358	5.11321	5.56371	8.05180	3.60883	1.23350	0.1213
0.4	0.99285	3.38502	2.85905	6.83512	1.32175	-1.37740	0.0597
0.5	-0.69177	2.01117	0.60408	8.88120	0.77296	-3.35182	0.0122
APE	2.87519	4.66276	5.70538	6.04579	3.09622	1.57887	-
313K							
0.0	1.97348	2.68338	6.27548	-2.07944	0.85960	2.58132	0.1384
0.1	3.97401	5.07975	7.52803	1.91006	2.95572	3.59560	0.1694
0.2	2.19203	3.72304	5.15718	1.88677	1.26218	1.00462	0.1117
0.3	0.79816	2.73587	3.16731	3.30991	0.49561	-1.02804	0.0665
0.4	-0.59356	1.71727	1.19827	5.59719	0.23418	-2.87919	0.0244
0.5	-2.82115	-0.17906	-1.56267	6.37768	-1.03682	-5.39296	-0.0305
APE	0.92049	2.62671	3.62727	2.83369	0.79508	-0.35311	-

formation of association in mixture through hydrogen bonded complexes[11]. As is evident from the APE values (Table 2), the best results are obtained by IDR followed by the results obtained from other theories.

Keeping in view of the aforementioned system, it can be thought that positive deviations in velocity are a result of (a) molecular association and (b) complex formation whereas negative deviations in velocity are due to molecular dissociation of associated species as a result of addition of inner solvent or an active solvent. The actual sign and magnitude of deviations depend upon relative strength of two opposite effects. The lack of smoothness in deviations is due to the interaction between the component molecules[12].

The deviations between theoretical and experimental values of ultrasonic velocities decrease with increase of temperature due to breaking of hetero and homo molecular clusters at higher temperatures [13]. On increasing the temperature, the ultrasonic velocity values decrease in the ternary liquid mixture. This is probably due to the fact that the thermal energy activates the molecule, which would increase the rate of association of unlike molecules. Based on the theoretical values of ultrasonic velocity; it is worthwhile to state that IDR method yield the best result at all temperatures. The magnitude of APE is in order:

IDR<NR<CFT <JM< IMR< FLT.

Conclusion:

Ultrasonic velocities predicted using NR, JM, IMR, FLT, CFT and IDR were compared with experimentally measured velocity values at different temperatures for the ternary mixture of tetrah ydrofuran(x_1)+hexane(x_2)+decane(x_3).From the magnitude APE, it may be concluded that IDR is best suited for the ternary mixture at all the temperatures. The observed deviation of theoretical values of velocity from the experimental values is attributed to the presence of molecular interactions in the system studied. Further the positive values of α in the system at all the temperatures clearly indicate the existence of strong tendency for the formation of association in mixture through hydrogen bonded complexes.

Acknowledgement:

I am very much thankful to Dr.G.Srinivasan, Asst. Prof. of Physics, Achariya College of Engineering Technology, Puducherry, for his continuous support and encouragement.

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