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# Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information: http://www.informaworld.com/smpp/title~content=t713646857

# Study of molecular interaction in ternary mixtures through ultrasonic speed measurements

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**To cite this Article** Ali, A., Nain, A. K., Sharma, V. K. and Ahmad, S.(2004) 'Study of molecular interaction in ternary mixtures through ultrasonic speed measurements', Physics and Chemistry of Liquids, 42: 4, 375 – 383 **To link to this Article: DOI:** 10.1080/00319100410001679882 **URL:** http://dx.doi.org/10.1080/00319100410001679882

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# STUDY OF MOLECULAR INTERACTION IN TERNARY MIXTURES THROUGH ULTRASONIC SPEED MEASUREMENTS

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(Received 30 September 2003)

Density ( $\rho$ ) and ultrasonic speed (u) of ternary liquid mixtures: acetonitrile (ACN) + 1-propanol + benzene, + toluene, + chlorobenzene and + nitrobenzene, and those of pure components, have been measured as function of composition at 303.15 K. Using experimental data, the values of isentropic compressibility ( $K_s$ ), intermolecular free length ( $L_f$ ), molar ultrasonic speed ( $R_m$ ), acoustic impedance (Z), excess isentropic compressibility ( $K_s^E$ ), excess free length ( $L_f^E$ ), excess volume ( $V^E$ ) and excess acoustic impedance ( $Z^E$ ) were computed. The increase or decrease of  $K_s$ ,  $L_f$ ,  $R_m$  and Z with composition indicates the presence of interaction between the component molecules in the mixtures. The excess functions  $K_s^E$ ,  $L_f^E$  and  $V^E$  are predominantly negative, while  $Z^E$  is almost positive. This further supports the presence of significant interactions between the component molecules in these mixtures. Theoretical values of ultrasonic speed have been calculated for all the four ternary mixtures at different compositions using free length theory (FLT), collision factor theory (CFT), Nomoto's (NOM) empirical relation and Van Dael and Vangeel (VDV) ideal mixing relation. A comparison of theoretical values of ultrasonic speed with those obtained experimentally reveals that, in general, CFT predicts the data reasonably well.

Keywords: Ultrasonic speeds; Ternary mixtures; Molecular interactions

## 1. INTRODUCTION

The study of molecular interaction between the components of binary and ternary liquid mixtures, using ultrasonic speed and thermodynamic parameters derived from it, has been the aim of several earlier workers [1–4]. Measurement of ultrasonic speed offers a convenient method for determining certain thermodynamic properties of liquids not easily obtained by other means [5]. In continuation of our systematic studies on non-aqueous binary and ternary liquid mixtures [6,7], we report here the results of our findings for the ternary mixtures: acetonitrile (ACN) + 1-propanol + benzene, + toluene, + chlorobenzene and + nitrobenzene, and those of pure components at 303.15 K over a wide composition range. The interactions involving  $\pi$ –H bonding between aromatic rings and proton donors, like alcohols, play a role in the structure

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of certain biomolecules [8] and this is a significant field of research [9]. Also, these liquids in the pure state as well as in the mixed form, with desired properties, find extensive applications as solvents in many chemical and industrial processes. ACN, benzene, toluene, chlorobenzene and nitrobenzene are aprotic due to the lack of hydrogen bonding, whereas 1-propanol is protic and hydrogen-bonded in the pure state. The molecules of acetonitrile and 1-propanol are highly polar and polar, respectively. Among the aromatics benzene molecules are non-polar, while those of toluene, chlorobenzene and nitrobenzene are weakly polar, polar and highly polar, respectively [10]. To our knowledge, no ultrasonic or volumetric study of these ternary liquid mixtures has been reported in the literature. Moreover, the substituent groups  $-CH_3$ , -Cl and  $-NO_2$ on the benzene ring are expected to influence the strength of interaction between the component molecules in these mixtures.

In order to investigate the nature of interactions we have measured the densities and ultrasonic speeds in the ternary mixtures: ACN + 1-propanol + benzene, ACN + 1-propanol + toluene, ACN + 1-propanol + chlorobenzene and ACN + 1-propanol + nitrobenzene, including those of pure liquids, as function of composition at 303.15 K. From the experimental data, the values of  $K_s$ ,  $L_f$ ,  $R_m$ , Z,  $K_s^E$ ,  $L_f^E$ ,  $V^E$  and  $Z^E$  have been calculated. The variation of these parameters with composition of mixtures is found to provide qualitative information regarding the nature and extent of intermolecular interaction in the liquid mixtures.

Theoretical evaluation of ultrasonic speed and its correlation with other thermodynamic properties in binary liquid mixtures using statistical and semi-empirical theories were made in the recent past [5,6,11-13]. However, relatively few data are available in the literature for ternary liquid mixtures. Ultrasonic speeds in all the four ternary liquid mixtures were theoretically evaluated using free length theory (FLT) [14], collision factor theory (CFT) [15] (CFT could not be applied to the system ACN + 1-propanol + nitrobenzene due to the non-availability of heat capacities of nitrobenzene in the literature), Nomato's empirical relation [16] and Van Dael and Vangeel ideal mixing relation [17]. Relative merits of these theories and relations were examined by comparing the theoretical values of ultrasonic speeds with those obtained experimentally.

## 2. EXPERIMENTAL

Acetonitrile, toluene and chlorobenzene (s.d. fine-chem, analytical reagent grade) were the same as in our previous study [6]. Benzene, nitrobenzene and 1-propanol (s.d. finechem., analytical reagent grade) were purified by the methods described in the literature [18,19]. Prior to use all liquids were stored over 0.4-nm molecular sieves to reduce the water content and were degassed. The solutions were prepared by mass in a dry box and were kept in special air tight bottles. The weighings were done on a Afcoset-ER-120A electronic balance with a precision of  $\pm 0.1$  mg.

The densities of pure liquids and ternary mixtures were measured using a singlecapillary pycnometer (made of Pyrex glass having a bulb capacity of  $8.0 \times 10^{-3}$  dm<sup>3</sup>). The capillary, with graduated marks, had uniform bore and can be closed using a well-fitting glass cap. The marks on the capillary were calibrated with triple-distilled water. The ultrasonic speeds in pure liquids and in their ternary mixtures were measured using a single-crystal variable-path ultrasonic interferometer at 3 MHz.

Component	ρ (	$g \mathrm{cm}^{-3}$ )	$u ({\rm ms^{-1}})$		
	Obsd.	Lit	Obsd.	Lit.	
Acetonitrile	0.7715	0.7708 [20]	1263.4		
1-Propanol	0.7978	0.7960 [21]	1192.0	1192.0 [21]	
Benzene	0.8684	0.8686 [23]	1281.7	1280.0 [24]	
Toluene	0.8581	0.8578 [23]	1289.3	1287.0 [24]	
Chlorobenzene Nitrobenzene	1.0957 1.1941	0.8580 [24] 1.0955 [23] 1.1935 [23]	1252.2 1444.3	1285.0 [25] 1252.0 [24] 	

TABLE I Densities ( $\rho$ ) and ultrasonic speeds (u) of pure components at 303.15 K

The temperature of the samples was maintained at  $303.15 \pm 0.02$  K in an electronically controlled thermostatic water bath. The purity of the chemicals was checked by comparing the measured densities and ultrasonic speeds of the pure liquids (Table I) with those reported in the literature [20–25].

# 3. RESULTS AND DISCUSSION

The experimental values of  $\rho$  and u were used to calculate the values of  $K_s$ ,  $L_f$ ,  $R_m$  and Z in all the four ternary mixtures using the following relations [6,7,13]:

$$K_s = u^{-2} \rho^{-1}$$
 (1)

$$L_f = K K_s^{1/2} \tag{2}$$

$$R_m = u^{1/3} V \tag{3}$$

$$Z = u\rho \tag{4}$$

where K is temperature-dependent constant [14] and V is the molar volume of the mixture. The values of  $\rho$ , u and those of  $K_s$ ,  $L_f$ ,  $R_m$  and Z are listed in Table II. It is evident that for all the systems investigated the values of  $K_s$  and  $L_f$  increase while those of  $R_m$ and Z show an opposite behaviour as the mole fraction x of ACN in the mixtures increases. The increase or decrease in these parameters with composition indicates the presence of interaction between the component molecules. Similar conclusion was also arrived at by others [13,26] during their ultrasonic study of liquid mixtures.

The parameters showing deviations form linear dependence of isentropic compressibility,  $K_s^E$ , intermolecular free length,  $L_f^E$ , molar volume,  $V^E$  and acoustic impedance,  $Z^E$  with composition are found to be sensitive towards intermolecular interaction. These parameters are derived from the following relations:

$$K_s^E = K_s - (x_1 K_{s1} + x_2 K_{s2} + x_3 K_{s3})$$
(5)

$$L_f^E = L_f - (x_1 L_{f1} + x_2 L_{f2} + x_3 L_{f3})$$
(6)

$$V^{E} = \left[ (M_{1}x_{1} + M_{2}x_{2} + M_{3}x_{3})/\rho \right] - \left[ (M_{1}x_{1}/\rho_{1}) + (M_{2}x_{2}/\rho_{2}) + (M_{3}x_{3}/\rho_{3}) \right]$$
(7)

$$Z^{E} = Z - (x_1 Z_1 + x_2 Z_2 + x_3 Z_3)$$
(8)

<i>x</i> <sub>1</sub>	<i>x</i> <sub>2</sub>	$(\text{kg m}^{-3})$	$(m s^{-1})$	$(10^{-10} \text{ m}^{K_s} \text{ N}^{-1})$	$(10^{-11} \text{ m})$	$R_m [10^{-4} \text{m}^3 \text{mol}^{-1} (\text{m s}^{-1})^{1.3}]$	$Z (10^6 \mathrm{kg}\mathrm{m}^{-2}\mathrm{s}^{-1})$
	1 prop	and $(2) + b$	mzene (3)			(	
0.1240	0.2177	$\frac{1101}{845}$	1253 1	7 5348	5 6973	8 8770	1.0591
0.1240	0.2177	840.4	1255.1	7.5428	5 7004	8 4260	1.0555
0.2300	0.2072	831.4	1255.7	7.6281	5 7325	8 0499	1.0333
0.3370	0.1970	823.1	1255.7	7.0201	5 7678	7 6985	1.0324
0.5151	0.1809	815.6	1257.8	7.8119	5 8012	7 3694	1.0218
0.5031	0.1736	804.3	1232.0	7.9687	5 8 5 9 1	7.0962	1.0218
0.5751	0.1750	796.4	1245.1	8 0917	5 9041	6.8165	0.9921
0.7315	0.1606	789.8	1243.7	8 1777	5 9354	6 5505	0.9827
0.7932	0.1548	785.6	1244.0	8.2254	5.9527	6.2862	0.9773
ACN (1	) + 1-prop	anol(2) + to	oluene (3)				
0.1391	0.2442	839.4	1258.3	7.5242	5.6933	9,9301	1.0562
0.2598	0.2282	831.2	1260.0	7.5780	5.7136	9.2979	1.0473
0.3656	0.2140	824.5	1258.6	7.6566	5.7432	8.7211	1.0377
0.4591	0.2016	817.9	1256.9	7.7392	5.7741	8.2099	1.0280
0.5423	0.1905	810.6	1254.3	7.8413	5.8121	7.7597	1.0167
0.6168	0.1806	803.4	1251.7	7.9445	5.8502	7.3557	1.0056
0.6840	0.1716	795.9	1245.7	8.0968	5.9060	6.9881	0.9915
0.7448	0.1635	788.9	1242.0	8.2174	5.9498	6.6553	0.9798
0.8001	0.1561	783.1	1241.1	8.2903	5.9761	6.3475	0.9719
ACN (1	)+1-prop	anol(2) + cl	hlorobenze	ene (3)			
0.1351	0.2373	1023.5	1229.4	6.4644	5.2771	9.4666	1.2583
0.2537	0.2228	1002.4	1231.4	6.5790	5.3237	8.8463	1.2344
0.3585	0.2099	982.3	1232.4	6.7027	5.3736	8.2853	1.2106
0.4519	0.1984	957.7	1233.0	6.8682	5.4395	7.8192	1.1808
0.5355	0.1881	931.2	1233.4	7.0591	5.5146	7.4155	1.1485
0.6110	0.1788	906.3	1233.8	7.2483	5.5880	7.0391	1.1182
0.6793	0.1704	878.0	1234.0	7.4795	5.6764	6.7231	1.0835
0.7415	0.1628	850.9	1235.1	7.7040	5.7610	6.4288	1.0509
0.7984	0.1558	826.1	1238.6	7.8905	5.8303	6.1469	1.0232
ACN (1	) + 1-prop	anol $(2) + n$	itrobenzen	ie (3)			
0.1357	0.2383	1082.2	1374.9	4.8882	4.5889	9.9629	1.4879
0.2545	0.2235	1050.3	1352.4	5.2057	4.7356	9.2802	1.4204
0.3595	0.2105	1013.8	1336.3	5.5238	4.8782	8.7294	1.3537
0.4529	0.1988	981.1	1325.7	5.7996	4.9984	8.2202	1.3006
0.5365	0.1884	951.5	1308.0	6.1429	5.1443	7.7246	1.2446
0.6118	0.1791	914.4	1296.6	6.5051	5.2937	7.3478	1.1856
0.6800	0.1706	879.2	1278.8	6.9552	5.4738	6.9820	1.1243
0.7420	0.1629	848.6	1268.3	7.3258	5.6177	6.6267	1.0763
0.7986	0.1559	813.5	1258.8	7.7576	5.7810	6.3370	1.0240

TABLE II Densities ( $\rho$ ), ultrasonic speeds (u), isentropic compressibilities ( $K_s$ ), intermolecular free lengths ( $L_f$ ), molar sound speeds ( $R_m$ ) and acoustic impedances (Z) for the ternary mixtures at 303.15 K

where x is the mole fraction of a component; subscripts 1, 2 and 3 refer to ACN (component 1), 1-propanol (component 2) and an aromatic compound (component 3: benzene or toluene or chlorobenzene or nitrobenzene), respectively; M stands for the molecular weight of a component.

The variations of  $K_s^E$ ,  $L_f^E$  and  $V^E$  with composition of the mixtures are given in Table III and have been qualitatively examined by considering the effects which influence these parameters. Mixing of the liquid components into each other will induce (i) the disruption of hydrogen bonds in 1-propanol and loss of dipolar association in ACN, chlorobenzene and nitrobenzene molecules, (ii) the formation of weak

$ \begin{array}{cccc} x_1 & & x_2 & & K_s & & L_t & & V^- \\ & & & & (10^{-11} \mathrm{m}^2 \mathrm{N}^{-1}) & & (10^{-12} \mathrm{m}) & & (10^{-6} \mathrm{m}^3 \mathrm{mol}^{-1}) \end{array} $	$(10^4 \mathrm{kg}\mathrm{m}^{-2}\mathrm{s}^{-1})$
	(IO KgIII S)
ACN $(1)$ + 1-propanol $(2)$ + benzene $(3)$	
0.1240 0.2177 -0.0073 0.0429 0.1303	-0.1474
0.2360 $0.2072$ $-0.1045$ $-0.3257$ $-0.1516$	0.8730
0.3376 $0.1976$ $-0.1148$ $-0.3665$ $-0.0353$	0.9686
0.4303 $0.1889$ $-0.1078$ $-0.3442$ $0.0126$	0.9518
0.5151 $0.1809$ $-0.0979$ $-0.3126$ $-0.0095$	0.9330
0.5931 $0.1736$ $-0.0144$ $-0.0114$ $0.2799$	0.1794
0.6650 0.1669 0.0410 0.1830 0.2833	-0.1934
0.7315 0.1606 0.0645 0.2589 0.1867	-0.3076
0.7932 0.1548 0.0541 0.2118 -0.0833	-0.0944
ACN $(1)$ + 1-propanol $(2)$ + toluene $(3)$	
0.1391 $0.2442$ $-0.0831$ $-0.2394$ $-0.0351$	0.6124
0.2598 0.2282 -0.1342 -0.4347 0.0961	1.0611
0.3656 $0.2140$ $-0.1475$ $-0.4882$ $0.0669$	1.2752
0.4591 $0.2016$ $-0.1460$ $-0.4874$ $0.0321$	1.3425
0.5423 $0.1905$ $-0.1162$ $-0.3822$ $0.0632$	1.1371
0.6168 $0.1806$ $-0.0777$ $-0.2469$ $0.0836$	0.8517
0.6840 0.1716 0.0163 0.0898 0.1274	0.1801
0.7448 0.1635 0.0841 0.3274 0.1292	-0.3094
0.8001 0.1561 0.1089 0.4082 0.0408	-0.4868
ACN $(1)$ + 1-propanol $(2)$ + chlorobenzene $(3)$	
0.1351 0.2373 -0.3792 -1.2754 -1.1647	3.9875
0.2537 0.2228 -0.4935 -1.7163 -1.5272	5.6903
0.3585 $0.2099$ $-0.5722$ $-2.0199$ $-1.9432$	6.9359
0.4519 0.1984 -0.5870 -2.0748 -1.9916	7.1881
0.5355 0.1881 -0.5577 -1.9642 -1.9010	6.8498
0.6110 $0.1788$ $-0.5142$ $-1.8070$ $-1.9349$	6.4217
0.6793 0.1704 -0.4149 -1.4456 -1.7296	5.3095
0.7415 0.1628 -0.3106 -1.0760 -1.6190	4.2090
$0.7984 \qquad 0.1558 \qquad -0.2340 \qquad -0.8179 \qquad -1.6745$	3.4005
ACN $(1) + 1$ -propanol $(2) + nitrobenzene (3)$	
0.1357 $0.2383$ $-0.8289$ $-2.8599$ $-0.1151$	4.9365
0.2545 $0.2235$ $-0.9283$ $-3.1836$ $-0.2734$	5.9567
0.3595 0.2105 -0.9784 -3.3393 -0.0625	6.2502
0.4529 0.1988 -1.0303 -3.5434 -0.1492	6.9455
0.5365 0.1884 -0.9803 -3.3448 -0.4612	6.8039
0.6118 0.1791 -0.8824 -2.9848 -0.2113	5.8321
0.6800 0.1706 -0.6715 -2.2112 -0.1033	4.1604
0.7420 $0.1629$ $-0.5184$ $-1.7060$ $-0.3284$	3.4107
0.7986 $0.1559$ $-0.2853$ $-0.9274$ $-0.2253$	1.8899

TABLE III Excess isentropic compressibilities  $(K_s^E)$ , excess intermolecular free lengths  $(L_f^E)$ , excess volumes  $(V^E)$  and excess acoustic impedances  $(Z^E)$  for the ternary mixtures at 303.15 K

to medium-strength hydrogen bonds between  $\pi$ -electrons of aromatic rings (benzene, toluene, chlorobenzene and nitrobenzene molecules) and H-atom of 1-propanol molecule, somewhat stronger hydrogen bond between nitrogen atom of ACN (with its lone pair of electrons) and H-atom of 1-propanol molecule, and dipole–dipole interaction between unlike molecules and (iii) interstitial accommodation of the component molecules into each other's structures. The first effect leads to an expansion in volume, resulting in positive  $K_s^E$ ,  $L_f^E$  and  $V^E$  values; positive values in these parameters may also occur where components interact less strongly. The remaining two effects contribute to contraction in volume, thereby, making  $K_s^E$ ,  $L_f^E$  and  $V^E$  values negative. It is clear from Table III that for the ternary mixtures investigated the values of  $K_s^E$  and  $L_f^E$  become

more negative as we move from benzene to nitrobenzene. This suggests that the combined effect of interaction between unlike molecules and interstitial accommodation of component molecules into each other's structure exceeds the structure-breaking effect between like molecules and also the strength of interaction between unlike molecules should follow the order: benzene < toluene < chlorobenzene < nitrobenzene. Our finding is in good agreement with the view proposed by Fort and Moore [26], according to which  $K_s^E$  and  $L_f^E$  become increasingly negative with increasing strength of interaction between unlike molecules in the liquid mixture.

A qualitative interpretation for the interaction between unlike molecules in the ternary mixtures may be proposed. Table III shows that the amount of 1-propanol is approximately same in all the four mixtures. As stated above, addition of benzene, toluene, chlorobenzene and nitrobenzene in ACN + 1-propanol causes the disruption of hydrogen bonds in 1-propanol and loosening of dipolar associations in ACN, toluene, chlorobenzene and nitrobenzene molecules, releasing several molecules of the component liquids for mutual interaction, possibly through (new) hydrogen bonds  $(-CN \cdots H-O)$  involving proton-acceptors -CN of  $ACN/\pi$ -electrons of benzene rings of the aromatic molecules and H-atom of -OH group of 1-propanol molecules. However, the strength of  $(\pi \cdot \cdot H - O)$  bond formed between aromatic compound and 1-propanol depends upon the nature of the substituent group present on the benzene ring of the aromatic compound. The presence of electron-repelling  $-CH_3$  group in toluene ( $C_6H_5CH_3$ ) molecule enhances the  $\pi$ -electron density of the ring, making the availability of  $\pi$ -electrons for electron-seeking H-atom of –OH group of 1-propanol easier, and accounting for stronger ( $\pi$ ···H–O) bond. On the other hand, –Cl atom in chlorobenzene ( $C_6H_5Cl$ ) and  $-NO_2$  group of nitrobenzene ( $C_6H_5NO_2$ ) being electronwithdrawing groups, the latter is the stronger electron-withdrawing group than the former one, tend to decrease the electron density of the benzene rings, making  $C_6H_5Cl$  and  $C_6H_5NO_2$  relatively poor electron donors towards electron-seeking Hatom of 1-propanol. This results in relatively weak  $(\pi \cdot \cdot \cdot H - O)$  bonds between chlorobenzene/nitrobenzene and 1-propanol molecules and the strength of such bonds should follow the sequence: toluene > chlorobenzene > nitrobenzene. For the present liquid mixtures, though the hydrogen-bonds between aromatic molecules and 1-propanol molecules are significant, it is equally significant to consider the dipole-dipole interactions between highly polar ACN molecule and those of aromatic molecules. As mentioned earlier, the polar character of the substituted aromatic molecules is in the order: toluene < chlorobenzene < nitrobenzene. Therefore, weak (ACN-toluene), medium-strength (ACN-chlorobenzene) and strong (ACN-nitrobenzene) dipolar interactions are obvious. Hence, the hydrogen bond and dipole-dipole interaction between unlike molecules jointly contribute towards the negative values of  $K_s^E$  and  $L_f^E$  in the present liquid mixtures, as is clear from Table III.

As expected, Table III shows that the values of  $V^E$  become more negative, while those of  $Z^E$  become increasingly positive, as we move from benzene to nitrobenzene. It clearly indicates the increased interaction between the component molecules of the mixtures. This again reinforces our view that the strength of interaction varies in the order: benzene < toluene < chlorobenzene < nitrobenzene. Interactions involving  $\pi$ -electrons of aromatic rings and proton of proton-donors forming  $\pi \cdot \cdot \cdot H$  bonds, as in benzene/toluene/nitrobenzene + 1-propanol, have been reported in the literature [9,27]. The importance of dipole–dipole interactions like ACN–dimethylsulphoxide [26] and dimethylformamide–aromatic molecules [25,28] for the study of liquid mixtures, all the liquids being polar aprotic in the pure state (as in our case), have been emphasized earlier.

A number of workers [11,13,29,30] have successfully carried out the theoretical evaluation of ultrasonic speed using empirical and semi-empirical relations [14-17] and compared the results with the experimental values of ultrasonic speed in binary liquid mixtures. Such an attempt has been useful in building theoretical models for liquids and their mixtures. With this view, theoretical values of ultrasonic speeds in ternary liquid mixtures: ACN + 1-propanol + benzene, + toluene, + chlorobenzene and +nitrobenzene at different compositions were evaluated using the following empirical and semi-empirical relations:

Free length theory (FLT) [14]:

$$u(\text{FLT}) = K / (L_f \rho^{1/2})$$
(9)

Collision factor theory (CFT) [15]:

$$u(\text{CFT}) = u_{\infty}(x_1S_1 + x_2S_2 + x_3S_3)[(x_1B_1 + x_2B_2 + x_3B_3)/V]$$
(10)

Nomoto's relation (NOM) [16]:

$$u(\text{NOM}) = \left[ (x_1 R_1 + x_2 R_2 + x_3 R_3) / (x_1 V_1 + x_2 V_2 + x_3 V_3) \right]^3$$
(11)

Van Dael and Vangeel ideal mixing relation (VDV) [17]:

$$u(VDV) = \{[(x_1/M_1u_1^2) + (x_2/M_2u_2^2) + (x_3/M_3u_3^2)](x_1M_1 + x_2M_2 + x_3M_3)\}^{-1/2}$$
(12)

The details of derivations and terms used may be obtained from the literature [5, 14–17,29,30]. Theoretically evaluated ultrasonic speeds from the aforesaid theories and relations together with the experimental values and percentage errors in the calculated values at 303.15 K are given in Table IV. A critical examination of the Table IV indicates that for the mixture ACN + 1-propanol + benzene minimum deviations are observed in the case of CFT, followed by NOM relation, then by FLT and VDV relation. For the mixture ACN + 1-propanol + toluene, again, CFT predicts the data with minimum deviations, followed by FLT, NOM and VDV relation. For both the mixtures ACN + 1-propanol + chlorobenzene and ACN + 1-propanol + nitrobenzene, ultrasonic speeds predicted by NOM relation show minimum deviations and agree closely with the experimental values, while maximum deviations are observed from FLT and VDV relation, respectively.

In general, it may be concluded that for all the four ternary mixtures investigated, CFT seems to provide the best results. This may be due to the presence of three empirical factors  $S_1$ ,  $S_2$  and  $S_3$ , the collision factors, contained in Schaaff's [15] Eq. (10). In fact, these factors are the correction terms and can be adjusted to give better results. This is in good agreement with the conclusion arrived at by Dewan *et al.* [29] and

TABLE IV Theoretical values of ultrasonic speed calculated from FLT, CFT, Nomoto's and Van Dael and Vangeel's equation along with the experimental values of ultrasonic speed and percentage error for the ternary mixtures at 303.15 K

<i>x</i> <sub>1</sub>	$x_2$	$(\mathrm{ms}^{-1})$	$(\mathrm{m}\mathrm{s}^{-1})$	$\frac{u_{CFT}}{(m s^{-1})}$	$\frac{u_{NOM}}{(\mathrm{m \ s}^{-1})}$	$(\mathrm{ms}^{-1})$	% error			
							FLT	CFT	NOM	VDV
ACN (1	) + 1-prop	anol (2) + b	enzene (3)							
0.1240	0.2177	1253.1	1248.4	1257.9	1262.0	1225.2	0.37	0.38	0.71	2.23
0.2360	0.2072	1256.0	1265.8	1261.3	1260.5	1212.3	0.78	0.42	0.36	3.48
0.3376	0.1976	1255.7	1256.6	1258.4	1259.1	1205.6	0.07	0.22	0.27	3.99
0.4303	0.1889	1254.3	1252.0	1256.7	1257.6	1203.6	0.18	0.19	0.27	4.04
0.5151	0.1809	1252.8	1252.5	1256.2	1256.2	1205.0	0.02	0.28	0.27	3.81
0.5931	0.1736	1249.1	1229.1	1250.0	1254.7	1209.2	1.60	0.07	0.45	3.20
0.6650	0.1669	1245.7	1227.1	1249.0	1253.3	1215.5	1.49	0.26	0.61	2.43
0.7315	0.1606	1244.3	1233.3	1250.1	1251.8	1223.5	0.88	0.46	0.61	1.67
0.7932	0.1548	1244.0	1255.3	1255.1	1250.4	1232.9	0.91	0.89	0.51	0.89
ACN (1	) + 1-prop	anol $(2) + t$	oluene (3)							
0.1391	0.2442	1258.3	1263.6	1262.4	1267.4	1199.0	0.42	0.33	0.72	4.71
0.2598	0.2282	1260.0	1253.6	1259.0	1265.3	1183.3	0.51	0.08	0.42	6.09
0.3656	0.2140	1258.6	1253.3	1258.0	1263.2	1177.4	0.42	0.05	0.37	6.46
0.4591	0.2016	1256.9	1253.7	1257.3	1261.2	1177.9	0.25	0.03	0.34	6.29
0.5423	0.1905	1254.3	1249.7	1255.7	1259.1	1182.9	0.37	0.11	0.39	5.69
0.6168	0.1806	1251.7	1246.3	1254.3	1257.1	1191.1	0.43	0.20	0.43	4.84
0.6840	0.1716	1245.7	1241.1	1252.5	1255.1	1201.8	0.37	0.54	0.75	3.52
07448	0.1635	1242.0	1239.2	1251.5	1253.0	1214.4	0.23	0.77	0.89	2.22
0.8001	0.1561	1241.1	1245.0	1252.5	1251.0	1228.4	0.31	0.92	0.80	1.02
ACN (1	) + 1-prop	anol $(2) + c$	hlorobenze	ene (3)						
0.1351	0.2373	1229.4	1300.9	1255.8	1240.9	1147.4	5.81	2.15	0.94	6.67
0.2537	0.2228	1231.4	1331.0	1264.6	1241.8	1131.1	8.09	2.70	0.85	8.14
0.3585	0.2099	1232.4	1370.5	1274.9	1242.7	1126.8	11.20	3.45	0.84	8.57
0.4519	0.1984	1233.0	1385.5	1279.4	1243.6	1130.6	12.33	3.76	0.86	8.31
0.5355	0.1881	1233.4	1388.0	1281.2	1244.5	1140.3	12.53	3.87	0.90	7.55
0.6110	0.1788	1233.8	1402.3	1285.1	1245.4	1154.6	13.66	4.16	0.94	6.42
0.6793	0.1704	1234.0	1393.1	1284.0	1246.3	1172.5	12.90	4.06	0.99	4.98
0.7415	0.1628	1235.1	1392.3	1284.5	1247.2	1193.5	12.73	4.00	0.98	3.36
0.7984	0.1558	1238.6	1409.2	1288.4	1248.1	1217.3	13.77	4.02	0.76	1.72
ACN (1	) + 1-prop	anol $(2) + n$	itrobenzen	e (3)						
0.1357	0.2383	1374.9	1291.3	_	1376.4	1188.7	6.08	_	0.11	13.54
0.2545	0.2235	1352.4	1289.5	_	1361.8	1152.9	4.65	_	0.70	14.75
0.3595	0.2105	1336.3	1256.1	_	1347.3	1137.0	6.01	_	0.82	14.91
0.4529	0.1988	1325.7	1254.9	_	1332.9	1133.7	5.34	_	0.54	14.48
0.5365	0.1884	1308.0	1278.8	_	1318.6	1139.1	2.23	_	0.81	12.91
0.6118	0.1791	1296.6	1251.8	_	1304.5	1151.0	3.46	_	0.61	11.23
0.6800	0.1706	1278.8	1241.6	_	1290.4	1168.1	2.91	_	0.91	8.66
0.7420	0.1629	1268.3	1265.0	_	1276.5	1189.5	0.26	_	0.64	6.21
0.7986	0.1559	1258.8	1260.4	-	1262.7	1214.7	0.12	-	0.31	3.50

Pandey and co-workers [5] that CFT makes accurate predictions of ultrasonic speeds in liquid mixtures.

# Acknowledgements

Ali and Nain are thankful to the Department of Science and Technology and Council of Scientific and Industrial Research, New Delhi for the award of major research project and research associateship, respectively.

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