



# Molecular interaction studies and theoretical estimation of ultrasonic speeds using scaled particle theory in binary mixtures of toluene with homologous nitriles at different temperatures

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## ABSTRACT

Densities,  $\rho$ , ultrasonic speeds,  $u$ , and viscosities,  $\eta$  of binary mixtures of toluene with acetonitrile (AN), propionitrile (PN) and butyronitrile (BN), including those of pure liquids are measured over the entire composition range at temperatures 298.15, 303.15 and 308.15 K, respectively. From these experimental data, excess intermolecular free length,  $L_f^E$ , the deviations in ultrasonic speed,  $\Delta u$ , excess acoustic impedance,  $Z^E$  and excess free energy of activation  $\Delta G^{*E}$  are calculated. The variation of these excess parameters indicates the presence of specific interactions between toluene and AN/PN/BN molecules, and the interactions follow the order: AN > PN > BN, i.e., the toluene–nitrile interaction decreases with increase in alkyl chain length. Moreover, the theoretical ultrasonic speeds are computed based on the scaled particle theory and compared with the experimentally measured values.

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## 1. Introduction

Molecular properties in liquid state are very useful for design calculations involving separations, heat transfer, mass transfer and fluid flow. Mixing volume effects play a pivotal role in many practical applications that include paints, varnishes and printing ink industries [1,2]. The present work is in continuation of our earlier studies [3,4] on understanding thermodynamic properties of binary mixtures whose components have relevant industrial applications.

Literature survey shows that molecular interaction of homologous series of nitriles with toluene using volumetric, viscometric and acoustic studies have not been reported except for the contradicting reports in AN+toluene binary mixture [5,6]. Abraham et al. [5] concluded the presence of strong interactions between AN–toluene molecules from negative deviations in isentropic compressibility studies. However, Ritzoulis et al. [6] reported contradicting weak interactions between the same AN–toluene binary mixture using excess viscosity values. Thus the above contradicting results promoted us to reinvestigate the molecular interactions in the above system other than toluene + PN/BN systems at three different temperatures.

Nitrile molecules are aprotic and highly polar with their dipoles oriented anti-parallel to each other and show strongly ordered structure due to strong dipole–dipole interactions [7]. The toluene molecules possess large quadrupole moments, causing an orientational ordering in this liquid. The orientational order is thought of as a partial alignment of neighbouring segments or possibly of whole molecules [8]. The binary mixtures containing aromatic hydrocarbons are interesting because they find applications in the studies of polymer phase diagrams and preferential interaction of polymers in mixed solvents [9,10]. Therefore, the study of intermolecular interactions in toluene + homologous aliphatic nitrile mixtures would be interesting owing to their industrial applications.

In this paper, we report the densities,  $\rho$ , ultrasonic speeds,  $u$  and viscosities,  $\eta$  of pure toluene, AN, PN and BN and those of their binary mixtures over the entire composition range at 298.15, 303.15 and 308.15 K. From these experimental data, the values of  $L_f^E$ ,  $\Delta u$ ,  $Z^E$  and  $\Delta G^{*E}$  are calculated and discussed in terms of molecular interactions between the unlike molecules. Furthermore, theoretical ultrasonic speeds of these mixtures are evaluated by considering the different shapes of the participating components using the scaled particle theory and compared with the experimental values.

## 2. Experimental

Toluene (Ranchem, India, purity >99.7%), AN, PN and BN (E. Merck, India, purity >99%) were purified by using the methods

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**Table 1**  
Comparison of experimental values of density,  $\rho$ , viscosity,  $\eta$  and ultrasonic speed,  $u$  of pure liquids with the corresponding literature values at different temperatures.

Liquids	T (K)	$\rho$ ( $10^3 \text{ kg m}^{-3}$ )		$\eta$ ( $10^{-3} \text{ N s m}^{-2}$ )		$u$ ( $\text{m s}^{-1}$ )	
		Exp	Lit	Exp	Lit	Exp	Lit
Toluene	298.15	0.8609	0.862055 [15]	0.5635	0.554 [16]	1299.8	1304 [17–19]
	303.15	0.8560	0.8566 [20]	0.5344	0.5284 [21]	1279.5	1282 [21]
	308.15	0.8516	0.85184 [20]	0.5091	0.5068 [22]	1260.7	1259 [23]
AN	298.15	0.7753	0.7764 [24]	0.3696	0.341 [25]	1271.3	1268.5 [25]
	303.15	0.7699	0.77122 [26]	0.3554	0.3501 [27]	1251.9	1258.64 [26]
	308.15	0.7647	0.7662 [28]	0.3414	0.3285 [5]	1231.7	1239 [5,29]
PN	298.15	0.7754	–	0.4107	–	1252.4	–
	303.15	0.7699	0.77191 [26]	0.3991	0.389 [12]	1232.7	1237.63 [26]
	308.15	0.7652	0.7646 [30]	0.3440	–	1213.7	1223.7 [30]
BN	298.15	0.7847	–	0.5463	–	1271.4	–
	303.15	0.7803	0.78172 [26]	0.5255	0.515 [12]	1252.2	1260 [31]
	308.15	0.7759	–	0.5049	–	1233.9	–

described in the literature [11,12] and only middle fractions were used in the experiment. All the chemicals were stored over 0.4 nm molecular sieves to remove water content and degassed just before use. The mixtures were prepared by mass and were kept in special airtight stopper glass bottles to avoid evaporation. The weightings were done by using an electronic balance (AND, HR series 300, Japan) with a precision of  $\pm 0.1$  mg. The uncertainty in the mole fraction was estimated to be less than  $\pm 1 \times 10^{-4}$ .

Densities of the pure liquids and their binary mixtures were measured by using a single capillary pycnometer (Borosil glass) having a bulb capacity of 10 mL. The capillary with graduated stem marks had a uniform bore and could be closed by a well-fitted glass cap. The marks on the capillary were calibrated with triple distilled water. The reproducibility in the density measurements was within  $\pm 0.1 \text{ kg m}^{-3}$  [13]. The ultrasonic speeds in pure liquids and in their binary mixtures were measured using a single-crystal variable-path multifrequency ultrasonic interferometer operated at 2 MHz. The reproducibility in the ultrasonic speed measurements was within  $\pm 0.03\%$ . The viscosities of pure liquids and their binary mixtures were measured by using Ubbelohde type suspended level viscometer with flow time of 174 s for triply distilled water at 308.15 K. As the flow time was greater than 100 s, the kinetic energy corrections were not necessary [14]. The viscometer containing the test liquid was allowed to stand for about 30 min in a thermostatic water bath so that the thermal fluctuations in viscometer were minimized. The time of flow was measured with an electronic stopwatch capable of recording  $\pm 0.01$  s. An average of four sets of flow times for each mixture was taken for the purpose of calculation of the viscosity. The overall experimental reproducibility was estimated to be  $\pm 2.0 \times 10^{-3} \text{ N s m}^{-2}$  [13]. The temperature of the test liquids during the measurements was maintained within an uncertainty of  $\pm 0.01$  K in an electronically controlled thermostatic water bath.

The reliability of experimental measurements of  $\rho$ ,  $u$  and  $\eta$  were ascertained by comparing the experimental data of pure liquids with the corresponding literature values (see Table 1).

### 3. Theory

The thermodynamic parameters like intermolecular free length ( $L_f$ ), acoustic impedance ( $Z$ ) and free energy of activation ( $\Delta G^*$ ) are calculated using the following standard relations [32,33]:

$$L_f = \frac{K}{u\rho^{1/2}} \quad (1)$$

$$Z = u\rho \quad (2)$$

$$\Delta G^* = RT \ln \left[ \frac{\eta V}{hN} \right] \quad (3)$$

where  $K$  is Jacobson's constant that depends upon temperature and is given by  $[K = (93.875 + 0.375T) \times 10^{-8}]$  [34],  $R$  is the universal gas constant,  $T$  being the absolute temperature.  $V$  is the molar volume  $[M_{\text{eff}}/\rho]$ ,  $M_{\text{eff}}$  is the effective molecular weight  $[M_{\text{eff}} = (x_1M_1 + x_2M_2)]$ , where  $M_1$ ,  $M_2$ ,  $x_1$  and  $x_2$  are the molecular weights and the mole fractions of toluene and nitriles, respectively.  $h$  and  $N$  are the Planck's constant and the Avogadro number, respectively. Instead of thermodynamic parameters, thermodynamic excess functions are found to be very sensitive towards mutual interactions between the component molecules of the binary mixtures. The sign and the extent of deviation of the functions from ideality depend on the strength of interactions between unlike molecules [35,36]. The excess intermolecular free length,  $L_f^E$ , excess acoustic impedance,  $Z^E$  and excess free energy of activation,  $\Delta G^{*E}$  are calculated using the general relation:

$$Y^E = Y - [x_1Y_1 + x_2Y_2] \quad (4a)$$

where  $Y$  represents  $L_f/Z$  or  $\Delta G^*$  of the mixture.

The deviations in ultrasonic speed,  $\Delta u$ , may be estimated using

$$\Delta u = u - [x_1u_1 + x_2u_2] \quad (4b)$$

The excess functions  $L_f^E$ ,  $\Delta u$ ,  $Z^E$  and  $\Delta G^{*E}$  are fitted to a Redlich–Kister type [37] polynomial equation:

$$P^E = x(1-x) \sum_{i=0}^n A_i(1-2x)^{i-1} \quad (5)$$

where  $P^E$  is  $L_f^E/\Delta u/Z^E$  and  $\Delta G^{*E}$ . The values of  $A_i$  are evaluated by using least squares method with all points weighed equally and the corresponding standard deviations  $\sigma(P^E)$  are calculated by using the relation:

$$\sigma(P^E) = \sum \left( \frac{(Y_{\text{cal}}^E - Y_{\text{exp}}^E)^2}{n-j} \right)^{1/2} \quad (6)$$

where  $n$  is the number of experimental data points and  $j$  is the number of  $A_i$  coefficients considered. The values of  $P_{\text{cal}}^E$  are obtained from Eq. (5) by using the best-fit values of  $A_i$  coefficients.

### 4. Results

The experimental values of densities,  $\rho$  and ultrasonic speeds,  $u$  and viscosities,  $\eta$  of binary mixtures of toluene with AN, PN and BN, over the entire composition range, expressed in terms of mole fraction,  $x_1$  of toluene at various temperatures are listed in Table 2. The values of coefficients  $A_0$ ,  $A_1$ ,  $A_2$ ,  $A_3$  and  $A_4$  along with standard deviation  $\sigma$  of fit for all the mixtures are listed in Table 3. The

**Table 2**

Densities,  $\rho$ , ultrasonic speeds,  $u$ , viscosities,  $\eta$ , deviations in ultrasonic speed,  $\Delta u$ , excess intermolecular free length,  $L_f^E$ , excess acoustic impedance,  $Z^E$  and excess free energy of activation,  $\Delta G^{*E}$  as functions of mole fraction,  $x_1$  of toluene for toluene + AN/PN/BN mixtures at different temperatures.

$x_1$	$\rho \times 10^{-3}$ (kg m <sup>-3</sup> )	$u$ (m s <sup>-1</sup> )	$\eta \times 10^3$ (N s m <sup>-2</sup> )	$\Delta u$ (m s <sup>-1</sup> )	$L_f^E$ (10 <sup>-11</sup> m)	$Z^E \times 10^{-5}$ (kg m <sup>-2</sup> s <sup>-1</sup> )	$\Delta G^{*E}$ (kJ mol <sup>-1</sup> )
Toluene + AN							
T = 298.15 K							
0.0000	0.7753	1271.3	0.3696	0.0000	0.0000	0.0000	0.0000
0.0506	0.7846	1273.8	0.3809	1.0579	-0.0248	0.0704	0.0553
0.1082	0.7941	1276.5	0.3940	2.1163	-0.0474	0.1360	0.1104
0.1704	0.8033	1279.3	0.4080	3.1436	-0.0667	0.1930	0.1584
0.2421	0.8126	1282.4	0.4241	4.2002	-0.0830	0.2415	0.2019
0.3228	0.8218	1285.7	0.4423	5.2002	-0.0953	0.2790	0.2373
0.4163	0.8307	1289.2	0.4625	6.0355	-0.1013	0.2978	0.2581
0.5288	0.8396	1292.0	0.4860	5.6292	-0.0957	0.2860	0.2593
0.6577	0.8475	1294.5	0.5098	4.4556	-0.0781	0.2374	0.2239
0.8089	0.8546	1296.7	0.5353	2.3464	-0.0470	0.1465	0.1465
1.0000	0.8609	1299.8	0.5635	0.0000	0.0000	0.0000	0.0000
T = 303.15 K							
0.0000	0.7699	1251.9	0.3554	0.0000	0.0000	0.0000	0.0000
0.0506	0.7790	1253.9	0.3653	0.6034	-0.0227	0.0630	0.0519
0.1082	0.7884	1256.3	0.3772	1.4137	-0.0446	0.1241	0.1058
0.1704	0.7975	1259.0	0.3900	2.3970	-0.0640	0.1782	0.1532
0.2421	0.8066	1261.8	0.4045	3.2180	-0.0790	0.2211	0.1950
0.3228	0.8157	1265.0	0.4211	4.1907	-0.0913	0.2560	0.2297
0.4163	0.8247	1268.2	0.4400	4.8101	-0.0968	0.2734	0.2520
0.5288	0.8338	1270.9	0.4614	4.4051	-0.0916	0.2635	0.2515
0.6577	0.8419	1273.6	0.4834	3.5475	-0.0753	0.2197	0.2166
0.8089	0.8493	1275.9	0.5069	1.6744	-0.0448	0.1348	0.1392
1.0000	0.8560	1279.5	0.5344	0.0000	0.0000	0.0000	0.0000
T = 308.15 K							
0.0000	0.7647	1231.7	0.3414	0.0000	0.0000	0.0000	0.0000
0.0506	0.7736	1233.4	0.3503	0.2326	-0.0208	0.0561	0.0501
0.1082	0.7829	1235.5	0.3609	0.6622	-0.0412	0.1114	0.1007
0.1704	0.7920	1238.0	0.3729	1.3584	-0.0599	0.1617	0.1486
0.2421	0.8014	1240.9	0.3864	2.1791	-0.0765	0.2068	0.1893
0.3228	0.8105	1244.3	0.4017	3.2388	-0.0895	0.2410	0.2228
0.4163	0.8197	1247.8	0.4193	4.0273	-0.0966	0.2610	0.2445
0.5288	0.8287	1250.7	0.4389	3.6648	-0.0907	0.2491	0.2424
0.6577	0.8369	1253.5	0.4591	2.7267	-0.0734	0.2053	0.2056
0.8089	0.8446	1256.3	0.4817	1.1419	-0.0436	0.1263	0.1312
1.0000	0.8516	1260.7	0.5091	0.0000	0.0000	0.0000	0.0000
Toluene + PN							
T = 298.15 K							
0.0000	0.7754	1252.4	0.4107	0.0000	0.0000	0.0000	0.0000
0.0668	0.7844	1257.2	0.4222	1.6337	-0.0226	0.0516	0.0286
0.1397	0.7936	1262.2	0.4346	3.1782	-0.0428	0.0991	0.0539
0.2164	0.8026	1267.3	0.4476	4.6426	-0.0598	0.1402	0.0752
0.3011	0.8117	1272.9	0.4617	6.2279	-0.0743	0.1757	0.0920
0.3905	0.8205	1278.2	0.4765	7.2903	-0.0830	0.1990	0.1035
0.4917	0.8294	1283.0	0.4927	7.2934	-0.0831	0.2029	0.1077
0.5989	0.8377	1287.1	0.5082	6.3121	-0.0743	0.1852	0.0976
0.7174	0.8457	1291.2	0.5247	4.7952	-0.0581	0.1476	0.0770
0.8540	0.8537	1295.2	0.5434	2.3204	-0.0317	0.0831	0.0436
1.0000	0.8609	1299.8	0.5635	0.0000	0.0000	0.0000	0.0000
T = 303.15 K							
0.0000	0.7699	1232.7	0.3991	0.0000	0.0000	0.0000	0.0000
0.0668	0.7788	1237.0	0.4087	1.1738	-0.0208	0.0455	0.0238
0.1397	0.7879	1241.7	0.4194	2.4620	-0.0400	0.0886	0.0466
0.2164	0.7968	1246.5	0.4306	3.6725	-0.0560	0.1252	0.0655
0.3011	0.8060	1252.0	0.4432	5.2085	-0.0712	0.1604	0.0821
0.3905	0.8149	1257.1	0.4561	6.1246	-0.0799	0.1827	0.0919
0.4917	0.8239	1262.1	0.4702	6.3884	-0.0813	0.1890	0.0947
0.5989	0.8323	1266.2	0.4842	5.4715	-0.0726	0.1725	0.0868
0.7174	0.8405	1270.4	0.4989	4.1257	-0.0570	0.1383	0.0676
0.8540	0.8486	1274.5	0.5158	1.8328	-0.0305	0.0763	0.0378
1.0000	0.8560	1279.5	0.5344	0.0000	0.0000	0.0000	0.0000
T = 308.15 K							
0.0000	0.7652	1213.7	0.3822	0.0000	0.0000	0.0000	0.0000
0.0668	0.7739	1217.6	0.3907	0.7604	-0.0186	0.0390	0.0212
0.1397	0.7830	1222.0	0.4004	1.7341	-0.0370	0.0786	0.0420
0.2164	0.7919	1226.7	0.4106	2.8292	-0.0530	0.1135	0.0591
0.3011	0.8011	1232.0	0.4220	4.1483	-0.0677	0.1461	0.0734
0.3905	0.8101	1237.1	0.4341	5.0465	-0.0771	0.1687	0.0833
0.4917	0.8191	1242.1	0.4475	5.2901	-0.0784	0.1744	0.0874

Table 2 (Continued).

$x_1$	$\rho \times 10^{-3}$ (kg m <sup>-3</sup> )	$u$ (m s <sup>-1</sup> )	$\eta \times 10^3$ (Ns m <sup>-2</sup> )	$\Delta u$ (m s <sup>-1</sup> )	$L_f^E$ (10 <sup>-11</sup> m)	$Z^E \times 10^{-5}$ (kg m <sup>-2</sup> s <sup>-1</sup> )	$\Delta G^{*E}$ (kJ mol <sup>-1</sup> )
0.5989	0.8276	1246.3	0.4606	4.4517	-0.0701	0.1594	0.0794
0.7174	0.8358	1250.5	0.4748	3.0822	-0.0537	0.1250	0.0628
0.8540	0.8440	1255.2	0.4911	1.3620	-0.0290	0.0693	0.0354
1.0000	0.8516	1260.7	0.5091	0.0000	0.0000	0.0000	0.0000
Toluene + BN							
T = 298.15 K							
0.0000	0.7847	1271.4	0.5463	0.0000	0.0000	0.0000	0.0000
0.0820	0.7927	1276.3	0.5484	2.5712	-0.0200	0.0411	0.0053
0.1673	0.8008	1280.6	0.5504	4.4487	-0.0355	0.0754	0.0090
0.2537	0.8086	1284.9	0.5522	6.2949	-0.0488	0.1052	0.0114
0.3488	0.8168	1289.2	0.5541	7.8941	-0.0595	0.1303	0.0130
0.4436	0.8245	1292.6	0.5559	8.6018	-0.0641	0.1425	0.0143
0.5435	0.8322	1294.9	0.5576	8.0646	-0.0614	0.1400	0.0133
0.6510	0.8398	1296.7	0.5592	6.8116	-0.0529	0.1231	0.0117
0.7590	0.8469	1298.0	0.5607	5.0444	-0.0401	0.0951	0.0093
0.8771	0.8541	1298.7	0.5622	2.3904	-0.0209	0.0512	0.0054
1.0000	0.8609	1299.8	0.5635	0.0000	0.0000	0.0000	0.0000
T = 303.15 K							
0.0000	0.7803	1252.2	0.5255	0.0000	0.0000	0.0000	0.0000
0.0820	0.7881	1256.5	0.5265	2.0614	-0.0177	0.0347	0.0039
0.1673	0.7961	1260.4	0.5276	3.6327	-0.0323	0.0654	0.0070
0.2537	0.8038	1264.5	0.5287	5.3740	-0.0455	0.0934	0.0096
0.3488	0.8120	1268.6	0.5299	6.8778	-0.0564	0.1180	0.0116
0.4436	0.8197	1272.2	0.5309	7.8897	-0.0627	0.1331	0.0123
0.5435	0.8273	1274.6	0.5317	7.5624	-0.0607	0.1316	0.0115
0.6510	0.8349	1276.5	0.5324	6.5277	-0.0531	0.1174	0.0097
0.7590	0.8419	1277.4	0.5329	4.4793	-0.0384	0.0867	0.0068
0.8771	0.8491	1278.3	0.5337	2.1552	-0.0201	0.0467	0.0036
1.0000	0.8560	1279.5	0.5344	0.0000	0.0000	0.0000	0.0000
T = 308.15 K							
0.0000	0.7759	1233.9	0.5049	0.0000	0.0000	0.0000	0.0000
0.0820	0.7836	1237.9	0.5053	1.8024	-0.0167	0.0310	0.0032
0.1673	0.7915	1241.7	0.5058	3.3164	-0.0312	0.0598	0.0056
0.2537	0.7992	1245.4	0.5064	4.7008	-0.0432	0.0845	0.0079
0.3488	0.8074	1249.3	0.5069	6.0522	-0.0539	0.1076	0.0087
0.4436	0.8151	1252.5	0.5074	6.7115	-0.0588	0.1197	0.0096
0.5435	0.8228	1254.7	0.5079	6.2342	-0.0565	0.1181	0.0089
0.6510	0.8304	1256.5	0.5082	5.1532	-0.0484	0.1035	0.0075
0.7590	0.8374	1257.8	0.5084	3.5588	-0.0353	0.0768	0.0061
0.8771	0.8446	1259.0	0.5088	1.5937	-0.0180	0.0402	0.0036
1.0000	0.8516	1260.7	0.5091	0.0000	0.0000	0.0000	0.0000

variations of  $L_f^E$ ,  $\Delta u$ ,  $Z^E$  and  $\Delta G^{*E}$  with mole fraction,  $x_1$  of toluene at 298.15 K, along with the smoothed values by using Eq. (5) are presented graphically in Figs. 1–4.

## 5. Discussion

### 5.1. Excess thermodynamic parameters

The increase in  $u$  values and decrease in  $L_f^E$  values with  $x_1$  (see Table 2) indicates significant interaction between the mixtures [38]. From Figs. 1–3, it is seen that  $L_f^E$  values are negative over the entire mole fraction range and at all temperatures investigated while  $\Delta u$  and  $Z^E$  show opposite trends indicating the presence of specific interactions between toluene and nitrile molecules [39]. The magnitude of  $L_f^E$  values for these mixtures follow the order: AN < PN < BN. In general, the observed  $L_f^E$ ,  $\Delta u$  and  $Z^E$  values depend on several factors, which are physical and chemical in nature [7,40]. The physical contributions, *i.e.*, dispersion forces and non-specific physical (weak) interactions that lead to positive  $L_f^E$  and negative  $\Delta u$  and  $Z^E$  values. Further physical contributions are also due to geometrical effects which allow molecules with very different sizes to fit into each other's structure resulting in negative  $L_f^E$  and positive  $\Delta u$  and  $Z^E$  values. Chemical contributions involve breaking up of the hydrogen-bonded structure(s), resulting in positive  $L_f^E$

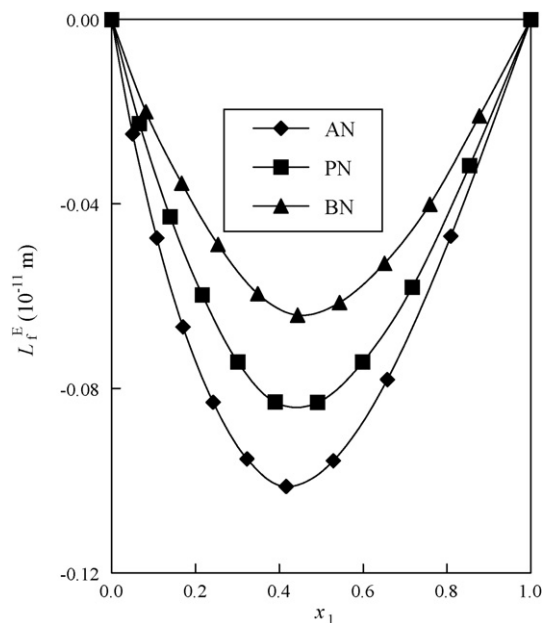


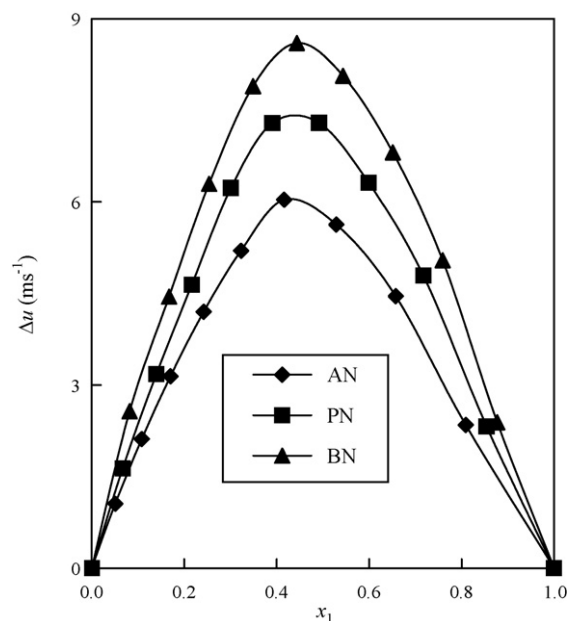
Fig. 1. Plots of  $L_f^E$  against mole fraction,  $x_1$  of toluene for binary mixtures of toluene with AN (◆), PN (■) and BN (▲) at 298.15 K.

**Table 3**  
Coefficients of  $A_i$  of Eq. (5) and standard deviations  $\sigma$  for the binary mixtures at different temperatures.

T/(K)	$A_0$	$A_1$	$A_2$	$A_3$	$A_4$	$\sigma$
<b>Toluene + AN</b>						
$L_f^E$ ( $10^{-11}$ m)						
298.15	-0.3925	-0.1439	0.0610	0.0338	-0.1016	0.0002
303.15	-3.7522	-1.2575	0.1710	-0.0151	0.0885	0.0033
308.15	-3.7286	-1.4687	1.0031	0.8731	-1.1115	0.0017
$\Delta u$ ( $\text{m s}^{-1}$ )						
298.15	2.3269	0.8987	-1.8804	-0.8306	1.8423	0.0040
303.15	1.8199	0.8393	-1.3329	-0.8933	0.5477	0.0056
308.15	1.5294	0.8992	-2.5448	-1.7581	2.2068	0.0036
$Z^E$ ( $10^5 \text{ kg m}^{-2} \text{ s}^{-1}$ )						
298.15	1.1675	0.3524	-0.1371	-0.0702	0.2093	0.0005
303.15	1.0746	0.2753	-0.0202	0.0665	-0.0717	0.0007
308.15	1.0202	0.3222	-0.2034	-0.1550	0.2146	0.0003
$\Delta G^{*E}$ ( $\text{kJ mol}^{-1}$ )						
298.15	1.0456	0.0873	0.0157	0.1337	-0.1308	0.0005
303.15	1.0081	0.0769	0.0181	0.1679	-0.2109	0.0002
308.15	0.9740	0.1201	-0.0589	0.0778	-0.1031	0.0006
<b>Toluene + PN</b>						
$L_f^E$ ( $10^{-11}$ m)						
298.15	-3.3150	-0.9782	1.1273	0.5582	-1.1849	0.0020
303.15	-3.2302	-0.8166	1.1601	0.4350	-0.8746	0.0033
308.15	-3.1180	-0.7629	1.1399	0.4831	-0.5938	0.0008
$\Delta u$ ( $\text{m s}^{-1}$ )						
298.15	2.9394	1.1156	-2.7312	-1.1301	2.7046	0.0043
303.15	2.5345	0.8433	-2.6032	-0.9310	2.0173	0.0064
308.15	2.0935	0.7558	-2.6086	-1.0289	1.8959	0.0030
$Z^E$ ( $10^5 \text{ kg m}^{-2} \text{ s}^{-1}$ )						
298.15	0.8080	0.1657	-0.2477	-0.1194	0.2386	0.0003
303.15	0.7512	0.1172	-0.2484	-0.0676	0.1763	0.0006
308.15	0.6942	0.0980	-0.2202	-0.0609	0.0819	0.0003
$\Delta G^{*E}$ ( $\text{kJ mol}^{-1}$ )						
298.15	0.4248	0.0735	-0.0954	-0.0159	0.0817	0.0003
303.15	3.7469	0.6070	-0.7022	-0.0953	0.0666	0.0031
308.15	3.4076	0.4328	-0.6483	-0.1313	-0.0577	0.0026
<b>Toluene + BN</b>						
$L_f^E$ ( $10^{-11}$ m)						
298.15	-2.5489	-0.4781	1.0541	0.0577	-0.9840	0.0026
303.15	-2.5014	-0.2586	1.2341	-0.1142	-0.9045	0.0041
308.15	-2.3441	-0.4228	1.3262	0.0525	-1.0476	0.0035
$\Delta u$ ( $\text{m s}^{-1}$ )						
298.15	3.4050	0.7668	-2.3038	-0.0561	2.0896	0.0050
303.15	3.1478	0.2629	-2.4107	0.3504	1.7628	0.0089
308.15	2.6439	0.6897	-2.3216	-0.1708	1.8549	0.0070
$Z^E$ ( $10^5 \text{ kg m}^{-2} \text{ s}^{-1}$ )						
298.15	0.5741	0.0522	-0.2314	-0.0100	0.1999	0.0006
303.15	0.5368	0.0092	-0.2626	0.0276	0.1761	0.0004
308.15	0.4838	0.0349	-0.2861	0.0073	0.2106	0.0006
$\Delta G^{*E}$ ( $\text{kJ mol}^{-1}$ )						
298.15	0.0554	0.0094	-0.0036	0.0043	0.0175	0.0000
303.15	0.0460	0.0120	-0.0224	-0.0063	0.0173	0.0000
308.15	0.0331	0.0076	-0.0155	-0.0055	0.0097	0.0001

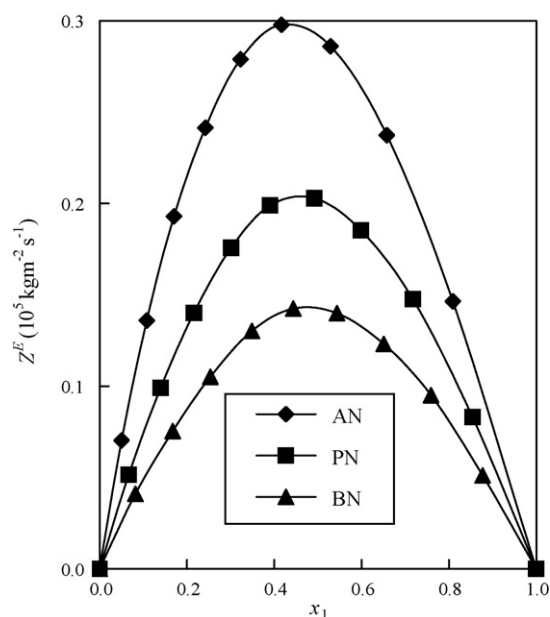
and negative  $\Delta u$  and  $Z^E$  values. However, specific interactions, such as the formation of hydrogen bonds, formation of charge-transfer complexes and strong dipole–dipole interactions between component molecules, result in negative  $L_f^E$  and positive  $\Delta u$  and  $Z^E$  values. Thus the observed negative trends in  $L_f^E$  and positive trends in  $\Delta u$  and  $Z^E$  values accounts for strong specific interaction between the unlike molecules of the mixtures.

A plausible qualitative interpretation of the behaviour of these mixtures with composition has been suggested. As stated earlier, the AN molecules have strong dipole–dipole interactions while toluene molecules possess large quadrupole moments, causing an



**Fig. 2.** Plots of  $\Delta u$  against mole fraction,  $x_1$  of toluene for binary mixtures of toluene with AN (♦), PN (■) and BN (▲) at 298.15 K

orientational order. Mixing of toluene with nitriles (AN/PN/BN) induces a decrease in the molecular order in toluene and dissociation of dipole–dipole association in nitriles, resulting in an expansion in volume, and hence, positive  $L_f^E$  and negative  $\Delta u$  and  $Z^E$  values. On the other hand, there is possibility of the electron donor–acceptor type (charge-transfer) interactions [41] between highly electronegative nitrogen of nitriles (acting as acceptor) and the  $\pi$ -electrons of ring of toluene molecules (acting as donor), resulting in negative  $L_f^E$  and positive  $\Delta u$  and  $Z^E$  values. Thus the observed negative  $L_f^E$  and positive  $\Delta u$  and  $Z^E$  values suggest the presence of significant donor–acceptor interactions between toluene and AN/PN/BN molecules. Ma et al. [41,42] have also reported similar type of donor–acceptor interactions between elec-



**Fig. 3.** Plots of  $Z^E$  against mole fraction,  $x_1$  of toluene for binary mixtures of toluene with AN (♦), PN (■) and BN (▲) at 298.15 K

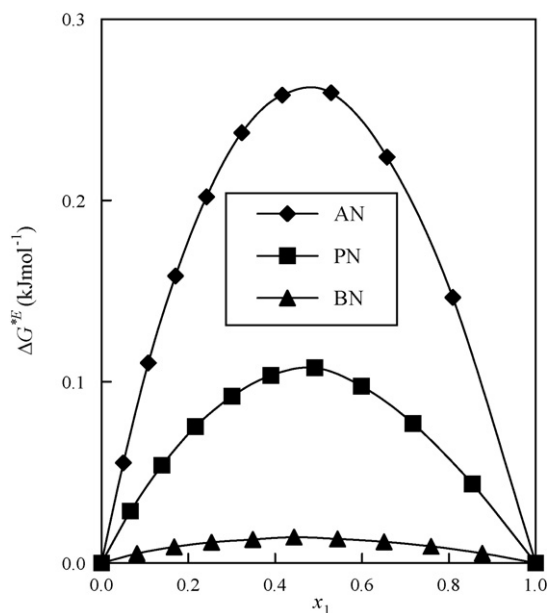


Fig. 4. Plots of  $\Delta G^{*E}$  against mole fraction,  $x_1$  of toluene for binary mixtures of toluene with AN (◆), PN (■) and BN (▲) at 298.15 K.

tronegative oxygen atom of sulpholane and  $\pi$ -electrons of the aromatic hydrocarbons.

Another contribution to negative  $L_f^E$  comes from the fitting of small AN/PN/BN molecules (molar volumes: AN = 52.947 cm<sup>3</sup> mol<sup>-1</sup>, PN = 71.034 cm<sup>3</sup> mol<sup>-1</sup>, BN = 88.072 cm<sup>3</sup> mol<sup>-1</sup> at  $T = 298.15$  K) into the voids created by bigger toluene molecules (molar volume = 107.03 cm<sup>3</sup> mol<sup>-1</sup> at  $T = 298.15$  K) [22]. Contributions arising from the fitting of smaller molecules into the voids available in the structure of bigger molecules were also considered by others [35,36,43] for interpreting excess parameter variations. Furthermore, the magnitude of  $L_f^E$  values at equimolar composition of these mixtures at 298.15 K follows the order: AN < PN < BN, which, in turn, indicates the order of the interactions between toluene and nitrile molecules.

It is interesting to note that the interaction between toluene and nitrile molecule in the mixtures decreases with increase in alkyl chain length of nitrile molecules. This may be due to the electron donor effect of alkyl group. Our observations are further supported by the results reported by Roy et al. [44] that large differences in dielectric constant of participating components of the mixture may result in negative  $L_f^E$  values. The dielectric constant of toluene is 2.379 at 296.15 K, while those of AN, PN and BN are 36.64, 29.70 and 24.83, respectively at 293.15 K [45]. The differences in dielectric constant values of toluene and nitrile molecules are large and may also result in negative  $L_f^E$  and positive  $\Delta u$  and  $Z^E$  values for the systems under study. Similar conclusions regarding the  $L_f^E$ ,  $\Delta u$  and  $Z^E$  values were reported for N,N-dimethylformamide + 2-methoxyethanol and N,N-dimethylformamide + 2-ethoxyethanol binary mixtures by Alisha et al. [46].

It has been reported earlier [47] that, the viscosity and hence the free energy of activation of a mixture strongly depends on entropy of mixture, which is related with liquid's structure and enthalpy (and consequently with molecular interactions between the components of the mixture). So, the excess free energy of activation variations are functions of molecular interactions as well as size and shape of molecules.

According to Fort and Moore [35], excess free energy of activation and deviation in viscosity tends to become more positive as the strength of interaction increases. In the present investiga-

Table 4  
Molecular assignment for different shapes.

Shape	Size	$\bar{R}$	$S$	$V_H$
Sphere	Radius = $a$	$a$	$4\pi a^2$	$4\pi a^3/3$
Cube	Side = $l$	$3l/4$	$6l^2$	$l^3$
Tetrahedron	Side = $l$	$(3l \arctan \sqrt{2})/2\pi$	$\sqrt{3}l^2$	$(\sqrt{2}/12)l^3$
Discs radius = $a$ and depth $l$				
Disc A	$l = a$	$(\pi + 1)a/4$	$4\pi a^2$	$\pi a^3$
Disc B	$l = a/4$	$(\pi + 0.25)a/4$	$5\pi a^2/2$	$\pi a^3/4$
Disc C	$l = a/2$	$(\pi + 0.50)a/4$	$3\pi a^2$	$\pi a^3/2$
Disc D	$l = a/10$	$(\pi + 0.10)a/4$	$11\pi a^2/5$	$\pi a^3/10$

tion, the positive trends in  $\Delta G^{*E}$  (Fig. 4) indicate the presence of specific interactions between unlike molecules, thereby complementing the results obtained through  $L_f^E$ ,  $\Delta u$  and  $Z^E$ . Similar positive  $\Delta G^{*E}$  values accounting strong interactions have been reported for DMSO + propionic acid and DMSO + n-butyric acid binary mixtures by Mishra et al. [33].

## 5.2. Scaled particle theory

The theoretical ultrasonic speeds of binary mixtures may be estimated based on some empirical, semi empirical and statistical models such as FLT, CFT, Nomoto and Vandeel Vangeal for the binary mixtures [48]. However, the common drawback of these theoretical models is that, the shapes of the participating species have not been taken into consideration. However, in scaled particle theory (SPT) [49] different shapes (such as sphere, cube, tetrahedral, disc A, disc B, disc C and disc D) of the participating components are considered and when the participating components have the correct shapes the theoretical ultrasonic speed estimated based on this model will give values close to the experimental values. Generally, the chemical structure of a liquid molecule is known but no definite shape has been attached to it [50]. Recently, Ghosh et al. [50] have used the scaled particle theory for the binary mixtures of 1,1,1-trichloroethane with 1-alkanols by considering different shapes such as spherical, cubical and tetrahedral. However, Kalidoss et al. [51] also have used the SPT for some binary mixtures and ternary liquid mixtures by considering seven shapes of the individual components that includes sphere, cube, tetrahedron, disc A, disc B, disc C and disc D (the shapes are assigned by some characteristic parameters as given in Tables 4 and 5, respectively). In this paper, theoretical ultrasonic speeds of the binary mixtures are estimated by assigning the above said seven shapes to the participating components and compared them with experimental speeds. Only when the participating molecules have particular shapes the theoretical values closely agrees with experimental ultrasonic speeds that will be determined by Chi-square fit ( $\chi^2$ ) [52].

The equation of state of fluid in the scaled particle theory is

$$\frac{p}{\rho_N k_B T} = \frac{1 + \alpha + \alpha^2}{(1 - \alpha)^2} \quad (7)$$

where  $\alpha = V_H \rho_N$ ,  $V_H$  is hard core volume,  $\rho_N$  [51] is number density and the other quantities have usual meaning [50].

Table 5  
Shape parameters.

Shape	$X = \bar{R}S/V_H$	$Y = \bar{R}/\sqrt[3]{V_H}$	$Z = S/\bar{R}^2$
Sphere	3.0000	0.6204	12.5664
Cube	4.5000	0.7500	10.6666
Tetrahedron	6.7035	0.9303	8.3247
Disc A	4.1416	0.7070	11.7218
Disc B	8.4790	0.9190	10.9244
Disc C	5.4624	0.7832	11.3712
Disc D	17.8274	1.1920	10.5253

**Table 6**  
Values of  $a$  (by Eq. (13)).

298.15 K				303.15 K				308.15 K			
TOL	AN	PN	BN	TOL	AN	PN	BN	TOL	AN	PN	BN
0.462	0.363	0.393	0.422	0.457	0.358	0.388	0.418	0.453	0.353	0.384	0.413
0.399	0.304	0.332	0.361	0.394	0.299	0.328	0.356	0.390	0.294	0.323	0.352
0.337	0.247	0.274	0.300	0.332	0.243	0.269	0.296	0.328	0.239	0.265	0.292
0.412	0.316	0.345	0.373	0.407	0.311	0.340	0.369	0.403	0.306	0.335	0.364
0.300	0.216	0.241	0.265	0.296	0.212	0.237	0.261	0.292	0.208	0.233	0.258
0.369	0.276	0.304	0.331	0.364	0.271	0.299	0.327	0.360	0.267	0.295	0.322
0.196	0.131	0.149	0.168	0.192	0.129	0.146	0.165	0.189	0.126	0.143	0.162

**Table 7**  
Ultrasonic speeds computed theoretically using SPT with behavioural shape having least Chi-square fit and experimentally measured values of the binary mixture TOL + AN at 298.15 K.

$x_1$	TOL + AN							
	$u_{exp}$	$u_{cal}$						
		Disc D + sphere	Disc D + cube	Disc D + tetra	Disc D + disc A	Disc D + disc B	Disc D + disc C	Disc D + disc D
0.0000	1271.3	1271.5	1271.3	1271.2	1250.4	1271.3	1271.4	1271.2
0.0506	1273.8	1265.8	1265.5	1267.7	1248.5	1265.0	1265.0	1265.6
0.1082	1276.5	1265.7	1264.7	1267.6	1251.1	1263.4	1263.7	1264.0
0.1704	1279.3	1268.5	1266.9	1269.8	1256.1	1265.0	1265.7	1265.3
0.2421	1282.4	1273.0	1271.0	1273.4	1262.5	1268.6	1269.7	1268.5
0.3228	1285.7	1278.2	1276.1	1278.0	1269.6	1273.5	1274.8	1273.1
0.4163	1289.2	1283.6	1281.6	1283.0	1276.8	1279.1	1280.4	1278.5
0.5288	1292.0	1288.9	1287.2	1288.1	1283.9	1285.1	1286.2	1284.5
0.6577	1294.5	1293.5	1292.2	1292.7	1290.2	1290.7	1291.5	1290.1
0.8089	1296.7	1297.1	1296.4	1296.6	1295.5	1295.6	1296.1	1295.2
1.0000	1299.8	1299.7	1299.7	1299.7	1299.7	1299.7	1299.7	1299.7
$\chi^2$		0.3798	0.5288	0.3174	2.5121	0.7545	0.6518	0.7578

SPT for mixtures of hard convex (not necessarily spherical) molecules gives the equation for mixture as follows [50,51]:

$$\frac{p}{\rho_N k_B T} = \frac{1}{(1 - V_{\rho_N})} + \frac{AB\rho_N}{(1 - V_{\rho_N})^2} + \frac{B^2 C \rho_N^2}{3(1 - V_{\rho_N})^3} \quad (8)$$

where

$$A = \sum x_i \bar{R}_i, \quad B = \sum x_i S_i, \quad C = \sum x_i \bar{R}_i^2, \quad V = \sum x_i V_{H_i} \quad (9)$$

$\bar{R}_i$ ,  $S_i$  and  $V_{H_i}$  are mean radius of curvature, surface area and volume, respectively, of a molecule of species  $i$ ,  $\rho_N$  is number density of mixture molecule, and  $x_i$  is the mole fraction.

Relating this with the equation:

$$\gamma \left( \frac{dp}{d\rho} \right)_T = u^2 \quad (10)$$

where  $u$  is the ultrasonic speed,  $\rho$  is molecular density and  $\gamma$  is the ratio of specific heats, we get:

$$\frac{Mu^2}{\gamma RT} = \frac{1}{(1 - V_{\rho_N})^2} + 2AB \frac{\rho_N}{(1 - V_{\rho_N})^3} + B^2 C \frac{\rho_N^2}{(1 - V_{\rho_N})^4} \quad (11)$$

Eq. (11) is used to evaluate the ultrasonic speeds in the binary mixtures.

For the case of pure liquids, the above equation is modified by introducing the dimensionless shape parameter,  $X = \bar{R}S/V_H$  and  $\alpha = V_H \rho_N$ :

$$\frac{Mu^2}{\gamma RT} = \frac{[1 + (X - 1)\alpha]^2}{(1 - \alpha)^4} \quad (12)$$

Solution to the above equation is obtained as [51]:

$$\alpha = K - \sqrt{K^2 + L - 1} \quad (13)$$

where  $K = 1 + L(X - 1)/2$  and  $L = \sqrt{\gamma RT/Mu^2}$ . The evaluated  $\alpha$  values are given in Table 6. Mean radius and the surface area of a

molecule can be written as

$$\bar{R} = YV_H^{1/3} \text{ and } S = Z\bar{R}^2 \quad (20)$$

where  $Y$  and  $Z$  are the parameters related to the shape of the molecule. If the molecule is assigned different shapes (see Table 4), then the corresponding values of  $X$ ,  $Y$  and  $Z$  (shape parameters) can be calculated (see Table 5).

In the present investigation, the theoretical speeds based on SPT is computed for the toluene–nitrile binary mixtures by considering different shapes, viz., sphere, cube, tetrahedron, disc A, disc B, disc C and disc D for both the participating components. Hence for a binary mixture there are 49 combinations of shapes at a particular temperature. By using  $\chi^2$  test, the best-fit combination of shapes of the participating component of molecules is arrived at. Chi-square

**Table 8**

Ultrasonic speeds computed theoretically using SPT with behavioural shape having least Chi-square fit and experimentally measured values of the binary mixture TOL + AN at 303.15 and 308.15 K.

$x_1$	TOL + AN			
	303.15 K		308.15 K	
	$u_{exp}$	$u_{cal}$ Disc D + tetra	$u_{exp}$	$u_{cal}$ Disc D + tetra
0.0000	1251.9	1251.8	1231.7	1231.6
0.0506	1253.9	1248.0	1233.4	1227.7
0.1082	1256.3	1247.4	1235.5	1227.0
0.1704	1259.0	1249.1	1238.0	1228.7
0.2421	1261.8	1252.4	1240.9	1232.1
0.3228	1265.0	1256.7	1244.3	1236.4
0.4163	1268.2	1261.5	1247.8	1241.4
0.5288	1270.9	1266.6	1250.7	1246.7
0.6577	1273.6	1271.4	1253.5	1251.8
0.8089	1275.9	1275.7	1256.3	1256.5
1.0000	1279.5	1279.4	1260.7	1260.6
$\chi^2$		0.34954		0.31716

**Table 9**  
Ultrasonic speeds computed theoretically using SPT with behavioural shape having least Chi-square fit and experimentally measured values of the binary mixture TOL + PN at 298.15, 303.15 and 308.15 K.

$x_1$	TOL + PN					
	298.15 K		303.15 K		308.15 K	
	$u_{\text{exp}}$	$u_{\text{cal}}$ Disc D + tetra	$u_{\text{exp}}$	$u_{\text{cal}}$ Disc D + tetra	$u_{\text{exp}}$	$u_{\text{cal}}$ Disc D + tetra
0.0000	1252.4	1252.3	1232.7	1232.6	1213.7	1213.6
0.0668	1257.2	1256.8	1237.0	1236.6	1217.6	1217.3
0.1397	1262.2	1261.8	1241.7	1241.3	1222.0	1221.8
0.2164	1267.3	1267.0	1246.5	1246.2	1226.7	1226.7
0.3011	1272.9	1272.4	1252.0	1251.5	1232.0	1232.0
0.3905	1278.2	1277.6	1257.1	1256.7	1237.1	1237.3
0.4917	1283.0	1282.9	1262.1	1262.1	1242.1	1242.7
0.5989	1287.1	1287.8	1266.2	1267.0	1246.3	1247.8
0.7174	1291.2	1292.3	1270.4	1271.6	1250.5	1252.6
0.8540	1295.2	1296.4	1274.5	1275.9	1255.2	1257.0
1.0000	1299.8	1299.7	1279.5	1279.4	1260.7	1260.6
$\chi^2$		0.0034		0.0040		0.0082

**Table 10**  
Ultrasonic speeds computed theoretically using SPT with behavioural shape having least Chi-square fit and experimentally measured values of the binary mixture TOL + AN at 298.15, 303.15 and 308.15 K.

$x_1$	TOL + BN					
	298.15 K		303.15 K		308.15 K	
	$u_{\text{exp}}$	$u_{\text{cal}}$ Disc D + disc C	$u_{\text{exp}}$	$u_{\text{cal}}$ Disc D + disc C	$u_{\text{exp}}$	$u_{\text{cal}}$ Disc D + disc C
0.0000	1271.4	1271.5	1252.2	1252.3	1233.9	1234.0
0.0820	1276.3	1276.3	1256.5	1256.6	1237.9	1237.9
0.1673	1280.6	1280.9	1260.4	1260.8	1241.7	1241.8
0.2537	1284.9	1285.0	1264.5	1264.7	1245.4	1245.5
0.3488	1289.2	1288.9	1268.6	1268.4	1249.3	1249.2
0.4436	1292.6	1292.1	1272.2	1271.5	1252.5	1252.4
0.5435	1294.9	1294.8	1274.6	1274.2	1254.7	1255.1
0.6510	1296.7	1297.0	1276.5	1276.5	1256.5	1257.5
0.7590	1298.0	1298.5	1277.4	1278.1	1257.8	1259.2
0.8771	1298.7	1299.5	1278.3	1279.1	1259.0	1260.3
1.0000	1299.8	1299.7	1279.5	1279.4	1260.7	1260.6
$\chi^2$		0.0012		0.0016		0.0037

test ( $\chi^2$ ) can be used to test the goodness of fit, which enables us to find whether the deviations of the theoretical values from the experimental ones are due to chance or really due to the inadequacy of the theory to fit the data.

The theoretical ultrasonic speeds based on SPT for the mixtures having liquids belonging to nitrile series with toluene at different temperatures are given in Tables 7–10, for the minimum values of  $\chi^2$ . For example, at 298.15 K, for toluene + AN binary mixture  $7 \times 7$  combinations of the different molecular shapes have been tried for the participating components and only when toluene bears the disc D shape the  $\chi^2$  value was found to be least. Hence as in Table 7, we have given the disc D shape for toluene and other possible shapes such as sphere, cube, tetrahedron, disc A, disc B, disc C and disc D for acetonitrile. From the  $\chi^2$  values (see Table 7), it is clear that when toluene + AN binary mixture takes the shapes of

disc D + tetrahedron, the ultrasonic velocity estimated based on SPT is found to be very close to the experimental values.

In order to see whether changes in temperature affects the shapes of the molecules in the mixture, the theoretical ultrasonic speeds of this mixture is evaluated at 303.15 and 308.15 K, respectively, for all the combination of the shape of the molecules (see Table 8), it is found that increase of temperature has no effect on the shape of the participating molecules.

Similarly for the toluene + PN binary mixture (Table 9), the theoretical ultrasonic speeds closely agrees well with the experimental values, when the participating molecules takes the shapes of disc D + tetrahedron at the studied temperatures.

From Table 10, it is further seen that, for the toluene + BN binary mixture, the participating molecules takes the shapes of disc D + disc C. Thus our theoretical analysis using SPT has proved that

**Table 11**  
Volume interaction ( $a$  and  $b$ ) and hard core correction ( $C$  and  $D$ ) parameters.

Binary mixture	298.15 K			303.15 K			308.15 K		
	$a$ (C)	$b$ (D)	Sign of $V_{\text{max}}^E$	$a$ (C)	$b$ (D)	Sign of $V_{\text{max}}^E$	$a$ (C)	$b$ (D)	Sign of $V_{\text{max}}^E$
TOL + AN	0.0174 (0.0072)	0.1076 (0.1176)	Positive	0.0222 (0.0112)	0.1107 (0.1235)	Positive	0.0251 (0.01)	0.1159 (0.122)	Positive
TOL + PN	0.0129 (–0.0109)	0.0480 (0.0082)	Positive	0.0143 (–0.0125)	0.0513 (0.0083)	Positive	0.0150 (–0.0211)	0.0545 (0.0096)	Positive
TOL + BN	0.0013 (–0.0035)	0.0133 (0.0004)	Positive	0.0017 (0.0009)	0.0152 (–0.0014)	Positive	0.0017 (–0.0133)	0.0172 (0.0029)	Positive



the temperature has no effect on the shapes of the participating components in all the three binary systems.

Using the volume interaction parameters (see Table 11) one can conclude that, in toluene + AN/PN binary mixtures, the nitrile molecules expand more than the toluene molecules while vice versa is noted in toluene + BN binary mixture.

Similar conclusions were drawn by Kalidoss et al. [51], using volume interaction parameters, for the binary mixtures of CCl<sub>4</sub> + benzene, CCl<sub>4</sub> + propanol, CCl<sub>4</sub> + butanol and benzene + butanol binary mixtures.

## 6. Conclusion

In this paper, density, ultrasonic speed and viscosity data are reported for binary mixtures of toluene and AN/PN/BN at three different temperatures. The excess parameter studies such as  $\Delta u$ ,  $L_f^E$ ,  $Z^E$  and  $\Delta G^{*E}$  indicate the presence of specific donor-acceptor (charge-transfer) interactions between toluene and nitrile molecules. Furthermore, theoretical ultrasonic speeds of these mixtures are evaluated by considering the different shapes of the participating components using the scaled particle theory.

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