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Thermodynamic and acoustic properties of binary mixtures of ethers. III. Diisopropyl ether or oxolane with o- or m-toluidines at 303.15, 313.15 and 323.15 K

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ABSTRACT

Densities ρ and speeds of sound u, of binary mixtures formed by o-toluidine or m-toluidine with diisopropyl ether (DIPE) or oxolane have been measured over the entire range of composition at a temperature of (303.15, 313.15 and 323.15) K and atmospheric pressure. The ρ and u values were used to calculate isentropic compressibilities κ_S, Rao's molar sound functions R, intermolecular free lengths L_f, specific acoustic impedances Z, excess molar volumes V_m^E, excess isentropic compressibilities κ_S^E, excess intermolecular free lengths L_f^E and excess specific acoustic impedances Z^E. The results have been used to investigate molecular interactions and structural effects in these mixtures. The speed of sound in present mixtures has been estimated using several empirical and theoretical models to determine their relative predicting ability in terms of pure component properties.

1. Introduction

The thermodynamic, acoustic and transport properties of non-electrolyte liquid–liquid mixtures provide information about type and extent of molecular interactions, and can be used for the development of molecular models for describing the behaviour of solutions [1–5]. They are also necessary for engineering calculation, research of mass transfer, heat transfer and fluid flow.

Amines are a very interesting class of compounds. Mixtures containing arylamines show very interesting features [6]. Systems with 1-alkanols are characterized by quite large positive deviations from Raoult's law [7,8], while linear amines + alkanol mixtures behave quite differently [9–11]. It has been reported that ether interacts with amine in their mixtures [12–14]. The formation of hydrogen bonds is assumed to occur between a primary or secondary amine group with weak proton donor ability and the unshared electron pairs on the oxygen atom of ether molecule. The arylamines are predominantly used as parent substances in the production of antioxidants, agricultural, pharmaceutical and rubber chemicals [15]. They are also used in manufacture of intermediate for synthetic dyes, and organic pigments especially for red color. It is well known that oxolane is an excellent solvent of polymers while diisopropyl ether is used as an oxygenate gasoline additive [16,17]. All this makes the study of ether-aromatic amine very interesting both industrially and theoretically. Therefore, we have undertaken systematic investigations of thermodynamic and acoustic properties of binary liquid mixtures involving aromatic amines with ethers at different temperatures.

In the previous papers [18,19] we have reported speeds of sound, isentropic compressibilities, Rao's molar sound functions, intermolecular free lengths, specific acoustic impedances, and various calculated excess properties of binary mixtures of oxolane or DIPE with aniline, N-methylaniline and N-ethylaniline at 303.15, 313.15 and 323.15 K. In this paper, we extend the work on mixtures of diisopropyl ether or oxolane with o-toluidine or m-toluidine. Nomoto model (NM) [20], Van Dael model (VM) [21], Ernst et al. model (EM) [22], impedance model (IM) [23], Schaaffs' collision factor theory (CFT) [24], Jacobson's free length theory (FLT) [25], and Prigogine–Flory–Patterson–Oswal theory (PFPOT) [26–29] have also been examined to estimate speeds of sound at different temperatures in the investigated binary mixtures.

2. Experimental

All chemicals used in this study were of analytical grade obtained from S.D. Fine-Chem. Ltd. The claimed mass fraction purity

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Table 1

Densities (ρ), speeds of sound (u), thermal expansion coefficients (α^{o}), and heat capacities ($C_{P}{}^{o}$) for pure liquids.

Liquid	T (K)	ρ (kg m^{-3})		u (m s^{-1})		α^{o}[a] (kK^{-1})	C_P^o (J mol^{-1} K^{-1})
		Expt.	Lit.	Expt.	Lit.		
DIPE	303.15	712.9	712.96[b] 713.06[d] 713.1[f] 713.20[g]	976	976.04[b] 974.9[e]	1.468	218[c]
	313.15	702.9	702.80[f] 702.59[g]	932	932.17[b]	1.489	222[h,i]
	323.15	691.9	691.533[b] 691.86[g]	889	888.61[b]	1.512	221[h,i]
Oxolane	303.15	876.9	877.0[j] 876.7[l]	1254	1254[j] 1255[l] 1256[m]	1.248	125[k]
	313.15	865.7	865.4[k] 870.5[o]	1207	1209[n] 1206.4[k]	1.265	128[k]
	323.15	854.8		1165		1.291	130[k]
o-Toluidine	303.15	990.1	990.2[h]	1579		0.848	218[h,i]
	313.15	981.7	983.2[p]	1539		0.855	220[h,i]
	323.15	973.3	973.8[p]	1501		0.863	222[h,i]
m-Toluidine	303.15	980.8	980.96[h]	1567		0.819	228[h,i]
	313.15	972.7		1533		0.826	230[h,i]
	323.15	964.6		1492		0.833	232[h,i]

[a] Derived from density data Ref. [30–35].
[b] Ref. [30].
[c] Ref. [36].
[d] Ref. [31].
[e] Ref. [37].
[f] Ref. [32].
[g] Ref. [33].
[h] Ref. [35].
[i] Temperature correction was estimated from group contribution method of Chueh-Swanson and Missenard [38].
[j] Ref. [39].
[k] Ref. [34].
[l] Ref. [40].
[m] Ref. [41].
[n] Ref. [42].
[o] Ref. [43].
[p] Ref. [44].

for the chemicals was >0.995. These liquids were dried over 4 Å molecular sieves and partially degassed prior to use. The purity of these experimental liquids was checked by comparing the observed densities and speeds of sound with those reported in the literature. The measured values are presented in Table 1 along with the available literature data.

The densities of pure liquids and the binary mixtures were measured by calibrated single stem capillary pycnometer having a bulb volume of about 10 cm^3 and capillary of internal diameter of 0.7 mm. The speeds of sound in pure liquids and in their binary mixtures were measured using single-crystal variable-path ultrasonic interferometer (Mittal Enterprises, New Delhi, Model: M-82) operating at 2 MHz. For all the measurements, temperatures were controlled by circulating water through an ultra thermostat JULABO F-25 (made in Germany) keeping fluctuations within ±0.02 K. The details of the experimental procedure have been described elsewhere [45]. The binary mixtures were prepared by mixing known masses of pure liquids in air tight stoppered bottles taking due precautions to minimize evaporation losses. All the mass measurements were performed on an electronic balance (Mettler-AE 240, Switzerland) accurate to ±0.05 mg. The samples for the measurements were immediately used after preparation. The uncertainty in density and speed of sound measurements was within 0.1 kg m^{-3} and 1 m s^{-1}.

3. Results and discussion

The results for the densities, speeds of sound, isentropic compressibilities, Rao's molar sound functions [46,47], specific acoustic impedances, intermolecular free lengths, excess molar volumes, and excess isentropic compressibilities for four binary mixtures of DIPE or oxolane with o-toluidine or m-toluidine at 303.15, 313.15, and 323.15 K are given in Tables 2–5.

From the values of densities and speeds of sound u, the isentropic compressibilities κ_S, Rao's molar sound functions R, specific acoustic impedances Z and intermolecular free lengths L_f were obtained using the relations

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

$$R = u^{1/3} V \tag{2}$$

$$Z = u\rho \tag{3}$$

$$L_f = K_{Jac}/u\rho^{1/2} = K_{Jac}\kappa_S^{1/2} \tag{4}$$

where molar volume $V = \Sigma(x_i M_i)/\rho$ in which x_i and M_i are the mole fraction and molecular mass of component i. $K_{Jac} = (91.368 + 0.3565T) \times 10^{-8}$ is temperature dependent Jacobson's constant [25]. The values of κ_S, R, and Z were uncertain within ±0.2% while L_f within 1%.

Excess molar volume V_m^E, excess isentropic compressibility κ_S^E, excess intermolecular free length L_f^E and excess specific acoustic impedance Z^E in each mixture were calculated with following expressions

$$Y^E = Y = Y^{id} \tag{5}$$

Table 2
Densities (ρ), speeds of sound (u), isentropic compressibilities (κ_S), Rao's molar sound functions (R), specific acoustic impedances (Z) and intermolecular free lengths (L_f), excess molar volumes (V_m^E) and excess isentropic compressibilities (κ_S^E) for DIPE + o-toluidine mixture at 303.15, 313.15 and 323.15 K.

x_1	ρ (kg m^{-3})	u (m s^{-1})	κ_S (TPa^{-1})	R^a	10^3Z (kg m^{-2} s^{-1})	10^2L_f (nm)	10^6 V_m^E (m^3 mol^{-1})	κ_S^E (TPa^{-1})
303.15 K								
0.0000	990.1	1579	405	1260	1563	3.997		
0.0717	968.9	1530	441	1270	1482	4.170	−0.517	−75
0.1513	946.3	1475	486	1280	1396	4.377	−1.097	−146
0.2389	922.0	1415	542	1290	1305	4.622	−1.681	−208
0.3255	898.8	1359	602	1301	1222	4.874	−2.234	−255
0.4206	873.5	1299	679	1312	1135	5.173	−2.713	−289
0.5248	845.6	1237	773	1327	1046	5.521	−3.015	−305
0.6250	817.9	1180	878	1344	965	5.885	−2.955	−297
0.7415	784.9	1116	1023	1367	876	6.352	−2.435	−255
0.8660	749.3	1049	1213	1395	786	6.916	−1.369	−165
1.0000	712.9	976	1473	1422	696	7.621		
313.15 K								
0.0000	981.7	1539	430	1260	1511	4.191		
0.0717	962.3	1491	467	1268	1435	4.369	−0.773	−88
0.1513	940.3	1437	515	1277	1351	4.586	−1.487	−172
0.2389	916.1	1378	575	1287	1262	4.845	−2.153	−246
0.3255	892.6	1320	643	1297	1178	5.124	−2.734	−300
0.4206	866.9	1259	728	1309	1091	5.451	−3.226	−340
0.5248	838.8	1197	832	1323	1004	5.829	−3.567	−360
0.6250	811.0	1139	951	1340	924	6.230	−3.546	−352
0.7415	777.6	1074	1115	1363	835	6.747	−3.010	−304
0.8660	741.0	1007	1331	1391	746	7.372	−1.793	−200
1.0000	702.5	932	1639	1421	655	8.180		
323.15 K								
0.0000	973.3	1501	456	1261	1461	4.396		
0.0717	955.7	1457	493	1267	1393	4.570	−1.041	−106
0.1513	934.4	1404	543	1275	1312	4.797	−1.909	−205
0.2389	910.4	1343	609	1284	1223	5.080	−2.678	−291
0.3255	886.4	1284	684	1294	1138	5.385	−3.267	−355
0.4206	860.2	1224	776	1307	1053	5.735	−3.765	−404
0.5248	831.6	1160	894	1321	965	6.154	−4.105	−429
0.6250	803.6	1103	1023	1338	886	6.584	−4.111	−424
0.7415	770.0	1038	1205	1361	799	7.147	−3.592	−374
0.8660	732.8	968	1456	1388	709	7.856	−2.296	−250
1.0000	691.9	889	1829	1420	615	8.804		

[a] Unit = m$^{10/3}$ s$^{-1/3}$ mol^{-1}.

where, Y represent either V, κ_S, L_f, and Z. The V_m^{id} for an ideal mixture was calculated from usual relation

$$V_m^{id} = \sum x_i V_i^O = \sum \frac{x_i M_i}{\rho_i} \tag{6}$$

κ_S^{id} for an ideal mixture were calculated from the relation recommended by Benson and Kiyohara [48] and Douheret et al. [49]

$$\kappa_S^{id} = \sum \phi_i \left\{ \frac{\kappa_{S,i}^o + TV_i^o(\alpha_i^o)^2}{C_{p,i}^o} \right\} - T(\sum x_i V_i^o) \left(\frac{\sum \phi_i \alpha_i^o 2}{(\sum x_i C_{p,i}^o)} \right) \tag{7}$$

L_f^{id} and Z^{id} for an ideal mixture were obtained as

$$L_f^{id} = K_{Jac}(\kappa_S^{id})^{1/2} \tag{8}$$

$$Z^{id} = \rho^{id} u^{id} = \left(\frac{\rho^{id}}{\kappa_S^{id}} \right)^{1/2} \tag{9}$$

in which the M_i, V_i^o, α_i^o and $C_{P,i}^o$ are respectively, the molar mass, molar volume, isobaric thermal expansion coefficient and molar isobaric heat capacity of pure component i, $\phi_i = x_i V_i / \Sigma x_j V_j$ is the volume fraction of i in the mixture, stated in terms of the unmixed components and $\rho^{id} = \sum \phi_i \rho_i^o$. The values of α^o and C_P^o used for these calculations are included in Table 1.

For compact and smooth representation, the values of u and κ_S were fitted to a polynomial equation of the form

$$u \text{ or } \kappa_S = \sum_{i=1}^{m} A_i X_1^{i-1} \tag{10}$$

The V_m^E, κ_S^E, L_f^E and Z^E were correlated by Redlich–Kister polynomial equation

$$Y^E = x_1(1-x_1)\sum_{i}^{n} B_i(1-2x_1)^i \tag{11}$$

where $Y^E = V_m^E,\ \kappa_S^E,\ L_f^E,$ and Z^E.

The coefficients A_i of Eq. (10) and B_i of Eq. (11) and corresponding standard deviations σ obtained from a least-squares fit with equal weights assigned to each point are given in Tables 6 and 7.

It is observed from Tables 2–5, that the values of speeds of sound, specific acoustic impedances decrease with mole fraction of DIPE or oxolane and also with the rise in temperature for all the mixtures studied. The values of isentropic compressibility, Rao's molar sound function, and intermolecular free length increase with the mole fraction of DIPE or oxolane and with the rise in temperature from 303.15 to 323.15 K. Figs. 1–4 show the dependence of V_m^E, κ_S^E, L_f^E, and Z^E on composition. The V_m^E, κ_S^E, and L_f^E are very large and negative for all the four studied mixtures over the entire mole fraction range, and their magnitude increases (i.e. decreases in absolute terms) with the rise in temperature from 303.15 to 323.15 K. Further, the values of V_m^E for both the DIPE mixtures are much more negative compared to both oxolane mixtures.

The observed values of V_m^E for presently investigated DIPE + toluidines mixtures are some of the largest negative values found for organic mixtures in the literature. In previous paper [19] also very large and negative, similar to present mixtures were observed for mixtures of DIPE with aniline or methyl aniline or ethylaniline. Other very large negative values of V_m^E reported

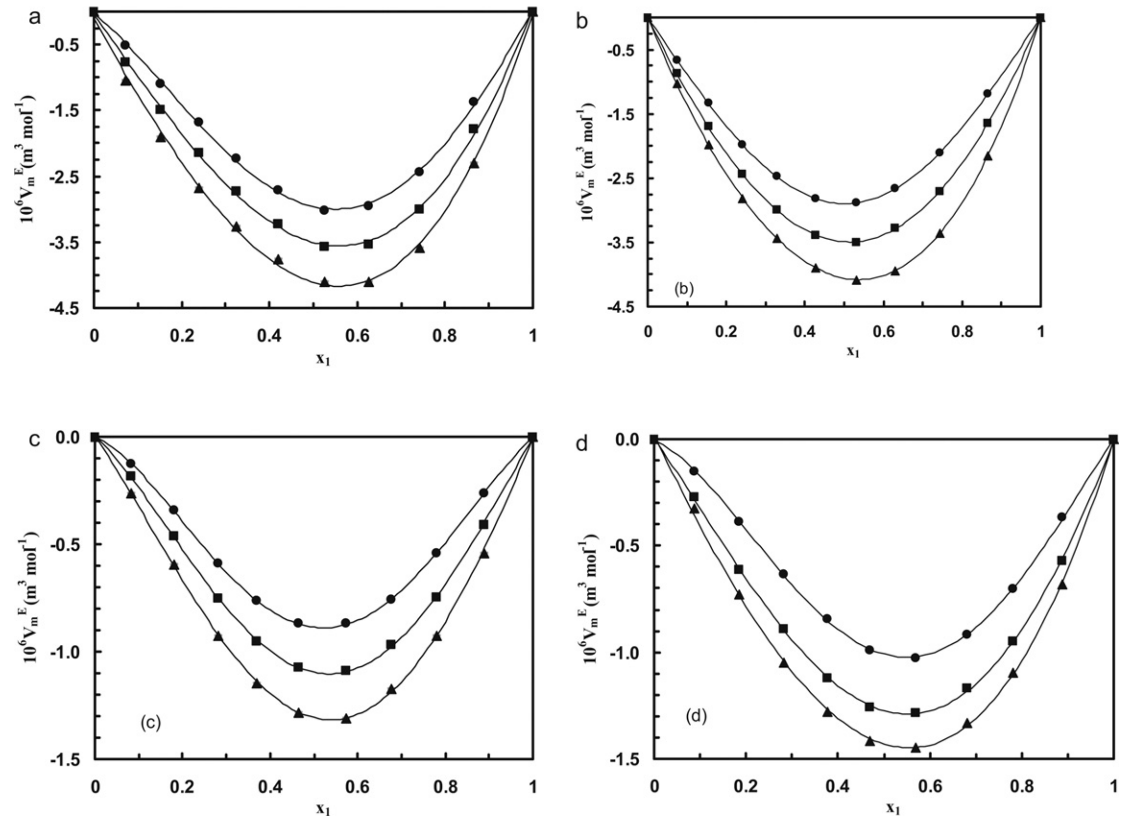

Fig. 1. Dependence of excess molar volumes on mole fraction of DIPE or oxolane, (a) DIPE + o-toluidine, (b) DIPE + m-toluidine, (c) oxolane + o-toluidine and (d) oxolane + m-toluidine at T = 303.15 K (●), 303.15 K (■), 323.15 K (▲). Solid lines have been drawn from Eq. (11) using coefficient given in Table 7.

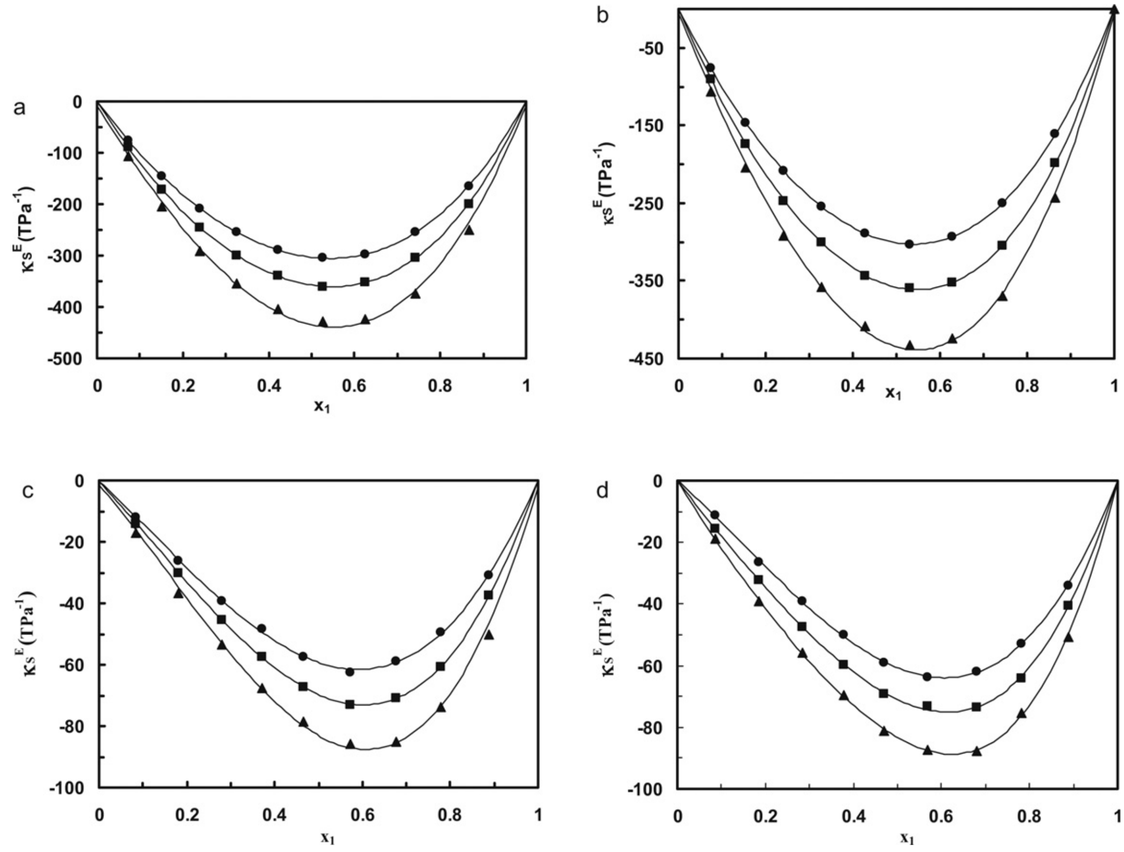

Fig. 2. Dependence of excess isentropic compressibilities on mole fraction of DIPE or oxolane, (a) DIPE + o-toluidine, (b) DIPE + m-toluidine, (c) oxolane + o-toluidine and (d) oxolane + m-toluidine at T = 303.15 K (●), 303.15 K (■), 323.15 K (▲). Solid lines have been drawn from Eq. (11) using coefficient given in Table 7.

Table 3
Densities (ρ), speeds of sound (u), isentropic compressibilities (κ_S), Rao's molar sound functions (R), specific acoustic impedances (Z) and intermolecular free lengths (L_f), excess molar volumes (V_m^E) and excess isentropic compressibilities (κ_S^E) for DIPE + m-toluidine mixture at 303.15, 313.15 and 323.15 K.

x_1	ρ (kg m^{-3})	u (m s^{-1})	κ_S (TPa^{-1})	$10^6 R$[a]	$10^3 Z$ (kg m^{-2} s^{-1})	$10^2 L_f$ (nm)	$10^6 V_m^E$ (m^3 mol^{-1})	κ_S^E (TPa^{-1})
303.15 K								
0.0000	980.8	1567	415	1269	1537	4.047		
0.0743	961.0	1515	453	1276	1456	4.228	−0.666	−76
0.1546	939.9	1462	498	1285	1374	4.431	−1.332	−147
0.2421	917.2	1404	553	1294	1288	4.670	−1.987	−209
0.3279	894.6	1350	613	1304	1208	4.918	−2.470	−255
0.4275	868.0	1289	693	1317	1119	5.229	−2.820	−289
0.5300	840.0	1230	787	1333	1033	5.571	−2.887	−303
0.6285	812.7	1175	891	1351	955	5.929	−2.667	−293
0.7424	781.2	1113	1033	1373	870	6.384	−2.112	−250
0.8651	747.8	1048	1218	1397	784	6.930	−1.195	−162
1.0000	712.9	976	1473	1422	696	7.621		
313.15 K								
0.0000	972.7	1533	438	1270	1491	4.226		
0.0743	954.3	1482	477	1276	1414	4.414	−0.879	−90
0.1546	934.0	1429	524	1283	1335	4.627	−1.702	−174
0.2421	911.5	1371	584	1291	1250	4.882	−2.448	−247
0.3279	888.9	1315	651	1301	1169	5.154	−2.994	−301
0.4275	862.1	1254	738	1314	1081	5.488	−3.385	−343
0.5300	834.0	1193	843	1329	995	5.865	−3.500	−360
0.6285	806.4	1138	958	1347	918	6.253	−3.286	−352
0.7424	774.5	1075	1117	1368	833	6.754	−2.715	−305
0.8651	740.1	1007	1332	1393	745	7.376	−1.650	−199
1.0000	702.9	932	1638	1420	655	8.178		
323.15 K								
0.0000	964.6	1492	466	1269	1439	4.443		
0.0743	946.9	1443	507	1274	1366	4.636	−1.033	−106
0.1546	927.0	1391	558	1281	1290	4.861	−1.981	−205
0.2421	904.6	1334	621	1289	1207	5.131	−2.822	−292
0.3279	881.9	1280	692	1299	1129	5.416	−3.431	−358
0.4275	855.0	1218	788	1312	1041	5.780	−3.890	−408
0.5300	826.9	1158	902	1327	958	6.182	−4.083	−433
0.6285	799.4	1101	1032	1344	880	6.613	−3.953	−424
0.7424	767.0	1036	1215	1365	795	7.175	−3.362	−370
0.8651	731.6	966	1465	1390	707	7.879	−2.160	−243
1.0000	691.9	889	1829	1420	615	8.804		

[a] Unit = m$^{10/3}$ s$^{-1/3}$ mol^{-1}.

in the literature include 2-methoxyethanol + tert-butylamine (−2.4 to −2.6 × 10^{-6} m^3 mol^{-1} [50]) and DMSO + cyclohexylamine (−3.4 × 10^{-6} m^3 mol^{-1}) [51].

On comparison of present V_m^E and κ_S^E of o-tuluidine and m-toluidine with aniline and methyl aniline, it is found that almost similar magnitude is found for aniline and toluidines while in methyl aniline mixtures magnitude of V_m^E and κ_S^E is slightly small compared to toluidines. Though toluidine and methyl aniline are isomers but toluidine being primary amine like aniline, their specific interactions with present ethers seem to be stronger than the methyl aniline, a secondary amine.

The over all behaviour of V_m^E and κ_S^E for the present mixtures can be envisaged as a resultant of opposite effects: (i) disruption of ether–ether interactions (ii) break down of dipolar and/or H-bonding self association in ether and aryl amine, (iii) aryl amine-DIPE cross association and dipole–dipole interactions, (iv) free volume effect, and (v) characteristic pressure P^* effect [52,53]. The estimated sum of free volume (fv) and characteristic pressure (P^*) contributions to the total V_m^E as per the Prigogine–Flory–Patterson (PFP) theory [26–28] is in the range from −2.26 to −2.73 × 10^{-6} m^3 mol^{-1} for DIPE + o-toluidine or m-toluidine; and from −0.45 to −0.55 × 10^{-6} m^3 mol^{-1} for oxolane + o-toluidine or +m-toluidine. It is clear that in very large negative values of V_m^E for DIPE + o-toluidine and +m-toluidine, the major contribution is due to the free volume and P^* effects, which include size, shape and conformation of the molecules involved. Still larger negative values of V_m^E than the free volume and P^* effects values for the present mixtures suggest that the dipole–dipole interactions (μ for DIPE/oxolane = 1.34/1.75 D, and for o-toluidines/m-toluidine ≈1.45/1.60 D [35]), and the cross-association between aromatic amine and DIPE/oxolane components dominate over the dispersive ether–ether interactions, breaking of dipolar order of aromatic amines as well as of DIPE/oxolane and the disruption of H-bonding in primary aromatic amines (toluidines). In the cross-association, the H-atom of the present aromatic amines interacts with O-atom of the DIPE/oxolane molecules. The negative V_m^E and κ_S^E values at equimolar compositions for common amine follow the order: DIPE > oxolane, while there is a marginal difference between the values of two isomers of toluidine. This difference is attributed to difference in free volume and internal pressure of two ethers under consideration.

As expected, the trend of negative L_f^E values (Fig. 3 and Table 7) is similar to κ_S^E in the studied mixtures. The negative values of L_f^E are generally observed in the mixtures with specific interactions between unlike molecules. The negative L_f^E values at equimolar compositions for common amine follow the order: DIPE > oxolane. Fig. 4 shows that Z^E is positive for all the studied mixtures. Specific acoustic impedance is a quantity, which depends on the molecular packing of the systems. The positive values of Z^E are in accordance with the presence of structureal effect and specific interactions between the unlike molecules [18,54].

The dependence of Rao's molar sound functions R on mole fractions x_1 is shown in Fig. 5. The Rao's molar sound function R decreases with mole fraction of DIPE in DIPE + toluidine mixtures while increases with mole fraction of oxolane in oxolane + toluidine. As per the Rao's theory, the R values are inde-

Table 4

Densities (ρ), speeds of sound (u), isentropic compressibilities (κ_S), Rao's molar sound functions (R), specific acoustic impedances (Z) and intermolecular free lengths (L_f), excess molar volumes (V_m^E) and excess isentropic compressibilities (κ_S^E) for oxolane + o-toluidine mixture at 303.15, 313.15 and 323.15 K.

x_1	ρ (kg m^{-3})	u (m s^{-1})	κ_S (TPa^{-1})	10^6R[a]	10^3Z (kg m^{-2} s^{-1})	10^2L_f (nm)	10^6 V_m^E (m^3 mol^{-1})	κ_S^E (TPa^{-1})
303.15 K								
0.0000	990.1	1579	405	1260	1563	3.997		
0.0828	984.0	1559	418	1229	1534	4.061	−0.126	−12
0.1818	977.0	1534	435	1190	1499	4.142	−0.344	−26
0.2807	969.9	1508	453	1151	1463	4.229	−0.592	−39
0.3704	962.6	1482	473	1115	1427	4.319	−0.765	−49
0.4652	953.7	1455	495	1080	1388	4.420	−0.871	−57
0.5732	941.7	1421	526	1039	1338	4.554	−0.869	−63
0.6764	928.4	1382	564	1001	1283	4.716	−0.758	−59
0.7791	913.3	1343	607	965	1227	4.893	−0.543	−50
0.8880	895.8	1300	661	926	1165	5.104	−0.265	−31
1.0000	876.9	1254	725	887	1100	5.348		
313.15 K								
0.0000	981.7	1539	430	1260	1511	4.191		
0.0828	975.9	1519	444	1228	1482	4.258	−0.184	−14
0.1818	969.2	1493	463	1189	1447	4.347	−0.465	−30
0.2807	962.2	1467	483	1149	1412	4.441	−0.754	−45
0.3704	954.9	1442	504	1114	1377	4.535	−0.953	−57
0.4652	945.9	1414	529	1078	1338	4.647	−1.076	−67
0.5732	933.8	1379	563	1038	1288	4.795	−1.092	−73
0.6764	920.1	1341	604	1000	1234	4.968	−0.966	−71
0.7791	904.7	1301	653	964	1177	5.164	−0.745	−61
0.8880	886.4	1255	716	925	1112	5.408	−0.413	−37
1.0000	865.7	1207	793	887	1045	5.690		
323.15 K								
0.0000	973.3	1501	456	1261	1461	4.396		
0.0828	968.0	1482	470	1228	1435	4.465	−0.264	−17
0.1818	961.5	1458	489	1189	1402	4.554	−0.596	−37
0.2807	954.6	1431	512	1149	1366	4.656	−0.924	−54
0.3704	947.3	1406	534	1114	1332	4.757	−1.149	−68
0.4652	938.2	1377	562	1077	1292	4.881	−1.286	−78
0.5732	925.9	1342	600	1037	1243	5.041	−1.308	−86
0.6764	911.9	1305	644	1000	1190	5.224	−1.174	−85
0.7791	896.0	1264	699	964	1133	5.441	−0.924	−74
0.8880	877.0	1219	767	926	1069	5.703	−0.542	−50
1.0000	854.8	1165	862	888	996	6.044		

[a] Unit = m$^{10/3}$ s$^{-1/3}$ mol^{-1}.

pendent of temperature (Tables 2–5). It is observed that there are slight negative deviations from the linear dependence on x_1 for all four binary mixtures at all the investigated temperatures. According to Rao's approach [46,47], the speed of sound is directly related to the strength of intermolecular energy. If the intermolecular energy were simply a consequence of additive non-bonding interaction, the Rao's molar sound function should predict additive behaviour. The fact that is not so implies some additional interactions in the mixtures compared with those in the simple liquids.

4. Estimation of speeds of sound

Recently, Gayol et al. [55] and Khammer and Shaw [56] described and tested several predictive methods for speed of sound in alkanol + n-alkanes mixtures and discussed the combing rules used in the different models. Glinski [57] discussed the additivity of sound velocity in twenty four randomly selected binary mixtures and found Nomoto model [20] based on Rao's hypothesis [47] provides results similar to those of Ernst et al. model [22] while the Van Dael model [21] often fails. For all three models large deviations were observed for mixtures with associating constituents. Here, the speeds of sound in the investigated binary mixtures have been estimated at 303.15, 313.15 and 323.15 K from the Nomoto model [20], Van Dael model [21], Ernst et al. model [22], impedance model [23], collision factor theory [24], intermolecular free length theory [25], and Prigogine–Flory–Patterson–Oswal theory [26–29]. The pertinent relations in these calculations and their theoretical basis have been outlined several times and will not be repeated here. PFPO model is the only model amongst the models considered here which has an interaction parameter X_{12}. Normally, the X_{12} is obtained from excess enthalpy data [27]. In absence of excess enthalpy data needed to determine interaction parameter X_{12}, we have determined speed of sound using X_{12} = 0 as well as X_{12} derived from equation [27]

$$X_{12} = P_1^*\left[1 - \left(\frac{P_2^*}{P_1^*}\right)^{1/2}\left(\frac{V_2^*}{V_1^*}\right)^{1/6}\right]^2 \tag{12}$$

where P^* and V^* are Flory's reduction parameter [27]. In order to determine relative predicting ability of various models, the standard percentage deviation $\sigma\%$ was calculated by considering percentage deviations for all mole fractions using the relation (13) and recorded in Table 8.

$$\sigma\% = \left[\frac{\sum\{100(u_{\text{expt}} - u_{\text{cal}})/u_{\text{expt}}\}^2}{n}\right]^{1/2} \tag{13}$$

where n represents number of data points.

The study of Table 8 reveals that the values of $\sigma\%$ for the NM, VM, EM, IM, CFT, FLT, and PFPOT are in the range from 0.5 to 3.6, 5.3 to 6.9, 1.1 to 6.7, 0.8 to 4.7, 0.6 to 3.2, 1.3 to 5.4 and 0.3 to 1.3 (0.1 to 2.5), respectively, for the four binary mixtures at investigated three different temperatures. The average values of standard deviations $\langle\sigma\%\rangle$ 1.9%, 2.8%, 1.9%, 2.8%, 0.9% for the NM, IM, CFT, FLT and PFPOT, respectively, are comparatively less than those found for other estimations. For EM and VM average $\sigma\%$ are 3.7% and 6.7%. Further it is observed, estimated results in oxolane mixtures are better than those for the mixtures involving DIPE. This is attributed to the fact that in oxolane mixtures interactions are not so complex as in case of DIPE mixtures. Considering the aver-

Table 5
Densities (ρ), speeds of sound (u), isentropic compressibilities (κ_S), Rao's molar sound functions (R), specific acoustic impedances (Z) and intermolecular free lengths (L_f), excess molar volumes (V_m^E) and excess isentropic compressibilities (κ_S^E) for oxolane + m-toluidine mixture at 303.15, 313.15 and 323.15 K.

x_1	ρ (kg m^{-3})	u (m s^{-1})	κ_S (TPa^{-1})	$10^6 R^a$	$10^3 Z$ (kg m^{-2} s^{-1})	$10^2 L_f$ (nm)	10^6 V_m^E (m^3 mol^{-1})	κ_S^E (TPa^{-1})
303.15 K								
0.0000	980.8	1567	415	1269	1537	4.047		
0.0864	975.3	1544	430	1234	1506	4.119	−0.154	−11
0.1853	969.2	1522	445	1195	1475	4.191	−0.386	−26
0.2831	963.0	1497	463	1155	1442	4.275	−0.634	−39
0.3776	956.4	1472	483	1117	1408	4.362	−0.846	−50
0.4693	949.0	1447	503	1081	1373	4.455	−0.989	−59
0.5689	939.3	1416	531	1043	1330	4.576	−1.027	−64
0.6803	926.2	1378	569	1001	1276	4.735	−0.919	−62
0.7808	912.4	1341	610	964	1224	4.903	−0.703	−53
0.8886	895.6	1300	661	926	1164	5.105	−0.368	−34
1.0000	876.9	1254	725	887	1100	5.348		
313.15								
0.0000	972.7	1533	438	1270	1491	4.226		
0.0864	968.0	1513	451	1235	1465	4.293	−0.272	−16
0.1853	962.6	1488	469	1194	1432	4.377	−0.612	−32
0.2831	956.4	1463	489	1154	1399	4.466	−0.890	−48
0.3776	949.7	1436	511	1116	1364	4.566	−1.121	−60
0.4693	942.0	1409	535	1080	1327	4.673	−1.261	−69
0.5689	931.9	1375	568	1041	1281	4.814	−1.287	−73
0.6803	918.4	1338	608	1000	1229	4.983	−1.169	−74
0.7808	904.3	1300	654	963	1176	5.169	−0.950	-64
0.8886	886.8	1255	716	925	1113	5.407	−0.572	−41
1.0000	865.7	1207	793	887	1045	5.690		
323.15								
0.0000	964.6	1492	466	1269	1439	4.443		
0.0864	960.1	1474	479	1234	1415	4.507	−0.324	−19
0.1853	955.0	1451	497	1193	1386	4.591	−0.730	−39
0.2831	948.9	1425	519	1153	1352	4.690	−1.051	−56
0.3776	941.9	1398	543	1115	1317	4.798	−1.279	−70
0.4693	933.9	1372	569	1079	1281	4.910	−1.415	−81
0.5689	923.6	1339	604	1041	1237	5.059	−1.449	−87
0.6803	909.8	1301	649	1000	1184	5.246	−1.330	−88
0.7808	895.3	1261	702	963	1129	5.456	−1.095	−75
0.8886	877.2	1217	770	925	1068	5.711	−0.681	−51
1.0000	854.8	1165	862	888	996	6.044		

[a] Unit = m$^{10/3}$ s$^{-1/3}$ mol^{-1}.

Table 6
Coefficients A_i of Eq. (10) along with standard deviations σ of binary mixture properties.

Properties	T/K	A_1	A_2	A_3	A_4	A_5	σ (Y^E)
DIPE + o-toluidine							
u (m s^{-1})	303.15	1579.3	−694.6	−15.9	266.5	−159.4	0.4
	313.15	1539.1	−662.8	−144.8	434.2	−233.7	0.5
	323.15	1501.8	−614.6	−358.4	758.7	−398.8	1.1
κ_S (TPa^{-1})	303.15	405.2	460.2	513.5	−325.3	418.9	0.3
	313.15	430.7	447.2	796.8	−719.8	683.4	1.1
	323.15	456.9	400.3	1295.2	−1547.4	1223.1	1.3
DIPE + m-toluidine							
u (m s^{-1})	303.15	1567.5	−717.1	183.4	−57.2		0.7
	313.15	1532.9	−679.7	−9.8	235.6	−147.2	0.6
	323.15	1492.1	−661.1	4.1	150.9	−97.3	0.5
κ_S (TPa^{-1})	303.15	415.6	466.3	443.4	−171.1	318.2	0.6
	313.15	438.1	461.0	685.7	−538.7	591.7	0.8
	323.15	466.3	482.5	763.0	−625.7	742.3	0.8
Oxolane + o-toluidine							
u (m s^{-1})	303.15	1579.3	−255.8	73.1	−272.1	129.4	0.9
	313.15	1539.4	−262.4	89.1	−282.3	123.0	0.6
	323.15	1501.3	−229.4	−56.1	−50.3		0.6
κ_S (TPa^{-1})	303.15	405.3	153.8	18.9	147.7		0.8
	313.15	429.9	178.2	−22.9	208.0		0.4
	323.15	456.2	154.0	167.7	−108.8	192.4	0.8
Oxolane + m-toluidine							
u (m s^{-1})	303.15	1566.6	−257.8	118.2	−304.6	131.8	0.7
	313.15	1533.0	−226.3	−68.9	−31.0		0.7
	323.15	1492.6	−213.5	−76.4	−37.3		0.8
κ_S (TPa^{-1})	303.15	415.6	161.3	−23.8	172.3		0.5
	313.15	437.6	149.2	105.5	−9.3	110.0	0.6
	323.15	465.8	135.4	217.6	−180.2	223.0	0.7

Table 7
Coefficients B_i of Eq. (11) along with standard deviations σ (Y^E) of excess properties of binary mixtures.

Properties	T/K	B_0	B_1	B_2	B_3	σ (Y^E)
DIPE + o-toluidine						
$10^6V_m^E$ (m^3 mol^{-1})	303.15	−11.876	4.006	3.409	−2.987	0.009
	313.15	−14.0615	4.762	1.055	−3.870	0.007
	323.15	−16.197	4.958	−2.259	−3.203	0.007
κ_S^E (TPa^1)	303.15	−1214.1	195.1	−112.8		0.3
	313.15	−1428.5	232.7	−188.1	62.7	0.8
	323.15	−1702.2	343.9	−322.6	74.3	0.5
10^3Z^E (kg m^{-2} s^{-1})	303.15	682.6	663.6	557.3		9.1
$10^2L_f^E$ (nm)	303.15	−4.199	−0.717			0.032
	313.15	−4.854	−0.810			0.042
	323.15	−5.716	−0.875			0.064
DIPE + m-toluidine						
$10^6V_m^E$ (m^3 mol^{-1})	303.15	−11.572	0.099	2.582		0.007
	313.15	−13.958	0.798	0.732		0.007
	323.15	−16.244	2.310	−1.055		0.006
κ_S^E (TPa^{-1})	303.15	−1205.3	180.2	−82.3		0.7
	313.15	−1433.7	241.4	−150.6	43.9	0.7
	323.15	−1718.5	357.8	−185.5		1.0
10^3Z^E (kg m^{-2} s^{-1})	303.15	672.3	642.7	499.4		7.2
$10^2L_f^E$ (nm)	303.15	−4.124	−0.704			0.026
	313.15	−4.825	−0.750			0.037
	323.15	−5.634	−0.792			0.043
Oxolane + o-toluidine						
$10^6V_m^E$ (m^3 mo^{-1})	303.15	−3.541	0.508	2.119		0.004
	313.15	−4.377	0.688	1.625	0.457	0.004
	323.15	−5.209	0.851	1.126	0.485	0.009
κ_S^E (TPa^{-1})	303.15	−236.3	94.9	−0.7		0.7
	313.15	−278.5	122.3	−9.7		0.5
	323.15	−324.9	168.1	−64.3		1.0
10^3Z^E (kg m^{-2} s^{-1})	303.15	306.4	8.9			2.4
$10^2L_f^E$ (nm)	303.15	−1.002	0.263			0.004
	313.15	−1.166	0.335			0.003
	323.15	−1.393	0.463			0.007
Oxolane + m-toluidine						
$10^6V_m^E$ (m^3 mol^{-1})	303.15	−4.031	1.351	1.861	−0.525	0.005
	313.15	−5.084	1.068	0.662	0.531	0.010
	323.15	−5.748	0.942	0.250	1.172	0.008
κ_S^E (TPa^{-1})	303.15	−243	120.7	−4.7		0.5
	313.15	−284.5	134.8	−35.9		0.6
	323.15	−332.9	167.8	−71.5		0.8
10^2Z^E (kg m^{-2} s^{-1})	303.15	309.6	−30.4			2.6
$10^2L_f^E$ (nm)	303.15	−1.024	0.376			0.003
	313.15	−1.212	0.382			0.004
	323.15	−1.429	0.458			0.009

Table 8
Standard percentage deviation (σ%) between experimental and estimated speed of sound using empirical or theoretical models for binary mixtures.

T/K	NM	VM	EM	IM	CFT	FLT	PFPOT	
							I[a]	II[b]
DIPE + o-toluidine								
303.15	2.6	5.5	5.4	4.6	2.9	2.5	2.4 0.4	
313.15	2.9	6.0	5.9	4.7	3.2	3.3	2.5 0.3	
323.15	3.5	6.9	6.7	4.6	3.2	4.3	2.3	0.4
DIPE + m-toluidine								
303.15	2.5	5.3	5.2	4.4	2.8	3.6	2.2	0.5
313.15	2.9	6.0	5.9	4.5	3.1	4.5	2.4	0.4
323.15	3.6	6.9	6.7	4.3	3.0	5.4	2.0	0.3
Oxolane + o-toluidine								
303.15	0.5	5.9	1.2	0.8	0.7	2.1	0.4	0.9
313.15	0.7	6.3	1.5	1.0	0.7	1.7	0.3	1.0
323.15	1.0	6.8	1.8	1.2	0.8	1.5	0.2	1.3
Oxolane + m-toluidine								
303.15	0.5	5.8	1.1	0.9	0.6	1.3	0.1	1.0
313.15	0.7	6.3	1.4	1.1	0.6	1.5	0.2	1.0
323.15	0.9	6.7	1.7	1.3	0.7	1.8	0.1	1.3
Average σ%	1.9	6.2	3.7	2.8	1.9	2.8	0.9	0.7

[a] X_{12} = 0.

[b] X_{12} = from Eq. (12).

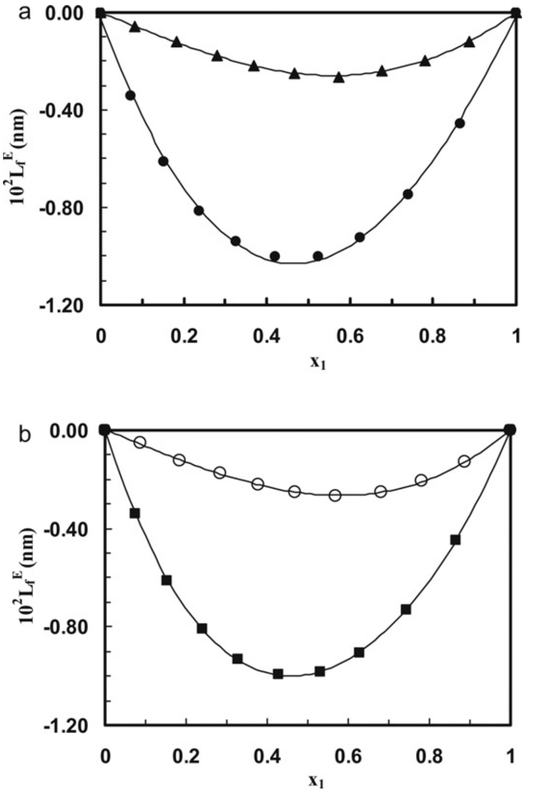

Fig. 3. Dependence of excess intermolecular free length on mole fraction of DIPE or oxolane at $T = 303.15$ K. (a) DIPE + o-toluidine (●) and oxolane + o-toluidine (▲). (b) DIPE + m-toluidine (■) and oxolane + m-toluidine (○). Solid lines have been drawn from Eq. (11) using coefficient given in Table 7.

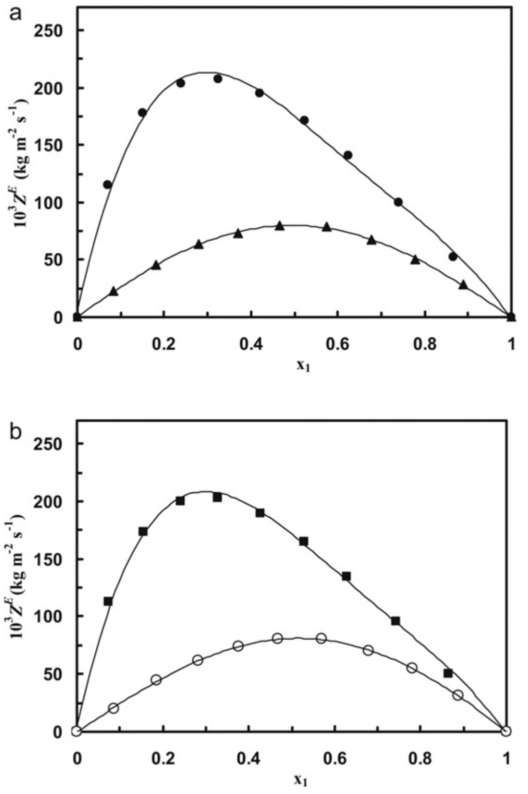

Fig. 4. Dependence of excess specific acoustic impedance on mole fraction of DIPE or oxolane at $T = 303.15$ K. (a) DIPE + o-toluidine (●) and oxolane + o-toluidine (▲). (b) DIPE + m-toluidine (■) and oxolane + m-toluidine (○). Solid lines have been drawn from Eq. (11) using coefficient given in Table 7.

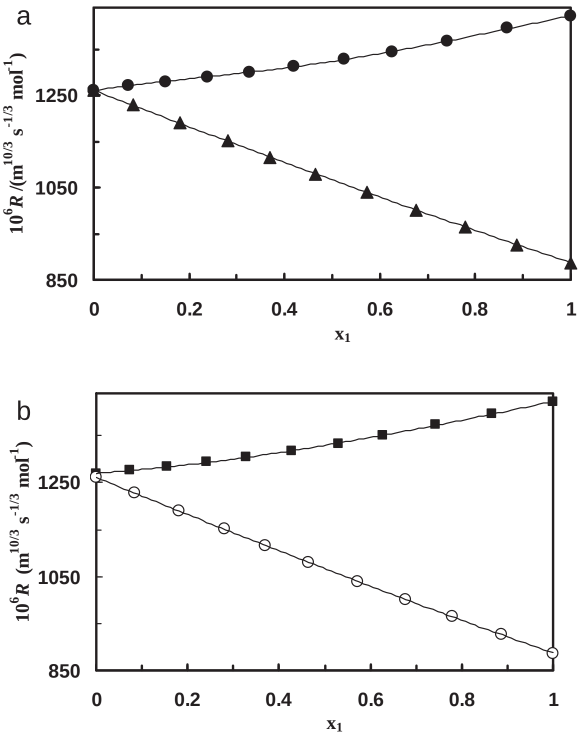

Fig. 5. Dependence of Rao's molar sound function on mole fraction of DIPE or oxolane at $T = 303.15$ K. (a) DIPE + o-toluidine (●) and oxolane + o-toluidine (▲). (b) DIPE + m-toluidine (■) and oxolane + m-toluidine (○).

age values of standard deviations, the estimation ability of speed of sound in the presently investigated mixtures follows the sequence PFPOT > CFT > ≅ NM > FLT ≅ IM > EM > VM. This indicates PFPOT provides best estimates of speed of sound in present mixtures It is also observed that speeds of sound in DIPE + toluidine mixtures estimated using X_{12} obtained by the equation [12] in the PFPO theory are better than that when $X_{12} = 0$ was taken, while reverse is the case for oxolane + toluidine mixtures.

5. Conclusions

The magnitude of large negative values of V_m^E, κ_S^E, and L_f^E and positive values of Z^E for binary mixtures of DIPE with o-toluidine or m-toluidine is much larger than that observed for oxolane mixtures at investigated temperatures 303.15, 313.15, and 323.15 K. This difference is attributed to the effect due to the difference in free volume and internal pressure of involved components. The specific interactions between unlike molecules through hydrogen bonding and dipole–dipole interactions between unlike molecules exist. The overall estimation ability of speed of sound in presently investigated mixtures follows the sequence PFPOT > CFT ≅ NM > FLT ≅ IM > EM > VM.

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