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Thermodynamic and acoustic properties of binary mixtures of oxolane with aniline and substituted anilines at 303.15, 313.15 and 323.15 K

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ABSTRACT

Speeds of sound u, 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, of three binary mixtures of oxolane (tetrahydrofuran) with aniline, N-methylaniline and N-ethylaniline have been reported over the entire range of composition at 303.15, 313.15 and 323.15 K. The excess values have been fitted to Redlich–Kister polynomial equation. The results have been analyzed in terms of molecular interactions between oxolane and anilines. The speeds of sound in present binary mixtures have been estimated from various empirical and theoretical models.

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 [1–6]. They are also necessary for engineering calculation, research of mass transfer, heat transfer and fluid flow. The increasing use of cyclic ethers and alkyl and aromatic amines in many industrial processes, as well as theoretical interest in the nature of associated solutions have greatly stimulated the need for extensive information on properties of mixtures involving these components. It has been reported that cyclic ethers interact with amines in their mixtures. Different volumetric and thermal effects are observed upon mixing because of the molecular interactions between cyclic ethers + amine [7–13]. 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 cyclic ether. Considerable systematic work on cyclic ether + alkylamine has been reported, whereas data on cyclic ether + aromatic amines is scanty [14,15]. Considering all these aspects we undertook investigations on the thermodynamic, acoustic and transport properties of binary mixtures involving oxolane and aromatic amines. Oxolane is used as a solvent in many chemical industries due to its proton accepting nature. The aniline is predominantly used [16] as parent substance in the manufacture of several chemical products and intermediates. It is also used in manufacture of synthetic dyes, drugs and as an accelerator in vulcanization of rubber. Secondary amines N-methylaniline and N-ethylaniline are used as a latent and coupling solvent. In the present paper, we report densities, speeds of sound, isentropic compressibilities, Rao's molar sound functions, intermolecular free lengths, specific acoustic impedances, and calculated excess functions of three binary mixtures of oxolane with aniline, N-methylaniline, and N-ethylaniline at 303.15, 313.15 and 323.15 K. This study will also provide a test of Nomoto's relation (NR) [17], Van Dael and Vangeel relation (VVR) [18], Junjie's relation (JR) [19], impedance relation (IR) [20], Schhaffs' collision factor theory (CFT) [21,22], Jacobson's free length theory (FLT) [23], and Progogine–Flory–Patterson–Oswal theory (PFPOT) [24–27] to estimate speed of sound in binary mixtures at different temperatures.

2. Experimental

All chemicals used in this study were of analytical grade and obtained from s.d.fine-chem., Ltd. The claimed mass fraction purity for the chemicals was >0.995. These liquids were dried over 4 Å molecular sieves and partially degassed prior to use. The purity of

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Table 1
Densities (ρ) and speeds of sound (u), thermal expansion coefficients (α), and heat capacities (C_P) for pure liquids.

Liquid	T (K)	ρ (kg m^{-3})		u (m s^{-1})		α (κK^{-1})	C_P (J mol^{-1} K^{-1})
		Expt.	Lit.	Expt.	Lit.		
Oxolane	303.15	877.3	877.0[a] 876.7[d]	1255.9	1256.3[b] 1255[d]	1.248	125[c]
	313.15	867.2	865.4[c] 870.5[f]	1211.7	1209[e] 1206.4[c]	1.269	128[c]
	323.15	856.6		1170.9		1.291	130[c]
Aniline	303.15	1012.8	1012.9[g] 1012.8[h]	1615.2	1614.5[i]	0.851[j]	191[k]
	313.15	1004.9	1004.4[h] 1004.6[m]	1582.6	1574.4[i]	0.858[j]	194[l]
	323.15	998.4		1558.2		0.866[j]	197[l]
N-methyl aniline	303.15	978.2	977.71[m] 978.1[h]	1548.3	–	0.816[j]	211[l]
	313.15	969.8	969.9[h] 969.6[m]	1512.4		0.822[j]	214[l]
	323.15	961.0	961.9[h]	1477.3		0.830[j]	218[l]
N-ethyl aniline	303.15	951.9	952.6[m]	1497.4	–	0.885[j]	227[l]
	313.15	944.3	944.2[m]	1462.2		0.893[j]	230[l]
	323.15	935.9		1430.5		0.902[j]	233[l]

[a] Ref. [28].
[b] Ref. [29].
[c] Ref. [30].
[d] Ref. [31].
[e] Ref. [32].
[f] Ref. [33].
[g] Ref. [34].
[h] Ref. [35].
[i] Ref. [36].
[j] Derived from density data from Ref. [37].
[k] Ref. [38].
[l] Estimated from group contribution method of Chueh-Swanson [39].
[m] Ref. [37].

these experimental liquids was checked by comparing the observed densities and velocities with those reported in the literature. The measured values are included in Table 1 along with the available literature values [28–38]. The agreement between the two is with in combined experimental error.

Airtight stoppered bottles were used for the preparation of the mixtures. The weight of the dry bottle was first determined. The less volatile component of the binary mixtures was introduced first in the sample bottle followed by second component, and the weight at each step was taken using an electronic balance (Mettler-AE 240, Switzerland) accurate to ±0.05 mg. The densities of pure liquids and the binary mixtures were measured by calibrated single stem capillary pycnometer. 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 the water through an ultra thermostat JULABO F-25 (made in Germany) keeping temperature fluctuations within ±0.02 K. The details of the experimental procedure have been described elsewhere [40]. 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 ρ, speeds of sound u, isentropic compressibilities κ_S, Rao's molar sound functions R [41], specific acoustic impedances Z and intermolecular free lengths L_f, excess molar volumes V_m^E and excess isentropic compressibilities κ_S^E for binary mixtures of oxolane with aniline, N-methylaniline and N-ethylaniline at 303.15, 313.15, and 323.15 K over the entire range of composition are given in Tables 2–4.

From the values of densities and speeds of sound, the isentropic compressibilities, Rao's molar sound functions, specific acoustic impedances and intermolecular free length were obtained using the relations

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

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

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

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

where $V = \Sigma(x_i M_i)/\rho$ in which x_i and M_i are the mole fraction and molecular mass of component i. $K_{Jac} = ((91.368 + 0.3565T)10^{-8})$ is temperature dependent Jacobson's constant [23]. 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 from ρ and κ_S of pure liquids and binary mixtures with following expression

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

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

$$V_m^{id} = \Sigma x_i V_i^o = \frac{\Sigma x_i M_i}{\rho_i} \tag{6}$$

κ_S^{id} for an ideal mixture was calculated from the relation recommended by Benson and Kiyohara [42] and Douheret et al. [43]

$$\kappa_s^{id} = \Sigma\phi_i \left\{ \frac{\kappa_{S,i}^o + TV_i^o(\alpha_i^o)^2}{C_{p,i}^o} \right\} - T(\Sigma x_i V_i^o) \left(\frac{\Sigma\phi_i \alpha_i^{o2}}{\Sigma x_i C_{p,i}^o} \right) \tag{7}$$

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 oxolane (1) + aniline (2) mixture at 303.15, 313.15 and 323.15 K.

x_1	ρ (kg m^{-3})	u (m s^{-1})	κ_S (T Pa^{-1})	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 (T Pa^{-1})
303.15 K								
0.0000	1012.8	1615	379	1079	1636	3.864		
0.0870	1004.4	1592	393	1061	1599	3.937	−0.206	−18
0.1803	994.8	1565	410	1043	1557	4.023	−0.388	−36
0.2735	984.8	1535	431	1024	1512	4.122	−0.558	−50
0.3573	975.4	1509	450	1007	1472	4.213	−0.685	−62
0.4556	964.1	1476	476	987	1423	4.333	−0.846	−71
0.5638	950.5	1438	509	965	1367	4.479	−0.936	−77
0.6708	935.0	1393	551	944	1303	4.661	−0.883	−71
0.8169	910.1	1334	617	919	1215	4.933	−0.523	−52
0.8812	898.7	1306	652	907	1174	5.071	−0.342	−37
1.0000	877.3	1256	723	887	1102	5.339		
313.15 K								
0.0000	1004.9	1583	397	1080	1590	4.028		
0.0870	997.5	1561	412	1062	1557	4.099	−0.318	−23
0.1803	988.2	1531	432	1042	1513	4.199	−0.552	−42
0.2735	978.5	1500	454	1022	1468	4.306	−0.771	−58
0.3573	969.4	1473	476	1005	1428	4.407	−0.951	−71
0.4556	957.8	1440	504	985	1379	4.535	−1.106	−83
0.5638	943.9	1402	539	964	1323	4.691	−1.195	−91
0.6708	928.7	1359	583	943	1262	4.878	−1.185	−89
0.8169	904.0	1299	655	917	1174	5.173	−0.868	−70
0.8812	892.2	1267	698	905	1131	5.338	−0.660	−49
1.0000	867.2	1212	785	886	1051	5.663		
323.15 K								
0.0000	998.4	1558	413	1081	1556	4.181		
0.0870	991.5	1537	427	1063	1524	4.255	−0.410	−27
0.1803	981.6	1510	447	1044	1483	4.351	−0.630	−52
0.2735	971.8	1478	471	1024	1436	4.468	−0.876	−71
0.3573	962.4	1450	495	1007	1395	4.578	−1.069	−87
0.4556	951.6	1417	523	986	1349	4.709	−1.329	−103
0.5638	937.9	1379	561	965	1293	4.875	−1.490	−114
0.6708	922.6	1334	610	943	1230	5.083	−1.517	−112
0.8169	898.5	1268	692	915	1140	5.414	−1.313	−91
0.8812	885.0	1237	738	905	1095	5.594	−0.962	−69
1.0000	856.6	1171	852	887	1003	6.007		

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 V_i^o, α_i^o and $C_{P,i}^o$ are, respectively, the molar volume, isobaric thermal expansion coefficient and molar isobaric heat capacity of pure component i, $\phi_i = x_iV_i/\Sigma x_jV_j$ is the volume fraction of i in the mixture, stated in terms of the unmixed components and $\rho^{id} = \Sigma\phi_i\rho_i^o$. The values of α^o and C_P^o used for these calculations are listed 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 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 were correlated by Redlich–Kister polynomial equation [44]

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

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 5 and 6.

It is observed from Tables 2–4, that the values of speeds of sound u, Rao's molar sound functions R, specific acoustic impedances Z decrease with mole fraction of oxolane and also with rise in temperature for all the systems studied. The values of κ_S and L_f increase with the mole fraction of oxolane and with the rise in temperature. The Figs. 1–4 shows the dependence of V_m^E, κ_S^E, L_f^E, and Z^E on composition. V_m^E and κ_S^E are negative for all the systems over the entire mole fraction range and their magnitude decreases with rise in temperature from 303.15 to 323.15 K. The minimum κ_S^E occurs at 0.6 mol fraction for all the systems.

For oxolane + aniline, speed of sound and excess molar volumes at 308.15 K have been reported by Deshpande et al. [15] and excess molar volumes at 298.15 K by Suri and Naorem [14]. The present value of equimolar excess molar volume for oxolane + aniline at 303.15 K is 0.896×10^{-6} m^3 mol^{-1} which is in between the values -0.916×10^{-6} m^3 mol^{-1} of Suri and Naorem [14] at 298.15 K and -0.875×10^{-6} m^3 mol^{-1} of Deshpande et al. [15] at 308.15 K. Considering the effect of temperature the agreement is very good. Our inter-polated values of excess isentropic compressibility of equimolar oxolane + aniline mixture at 308.15 K is -80.2 T Pa^{-1} while Deshpande et al. [15] reported -63 T Pa^{-1}. For other two mixtures no work on either speed of sound or excess molar volumes at any temperature seems to have been reported in the literature.

The overall behaviour of V_m^E and κ_S^E 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-

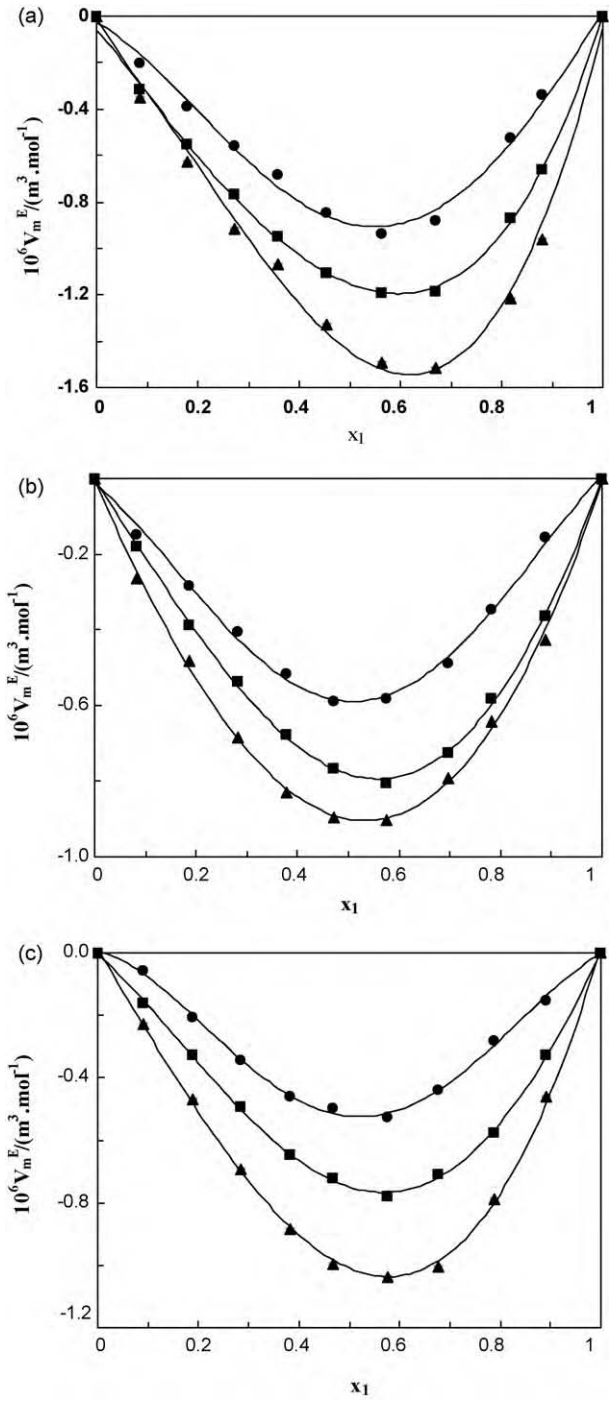

Fig. 1. Dependence of excess molar volumes on mole fraction of oxolane, (a) oxolane + aniline, (b) oxolane + N-methylaniline and (c) oxolane + N-ethylaniline at T = 303.15 K (●), 303.15 K (■), and 323.15 K (▲).

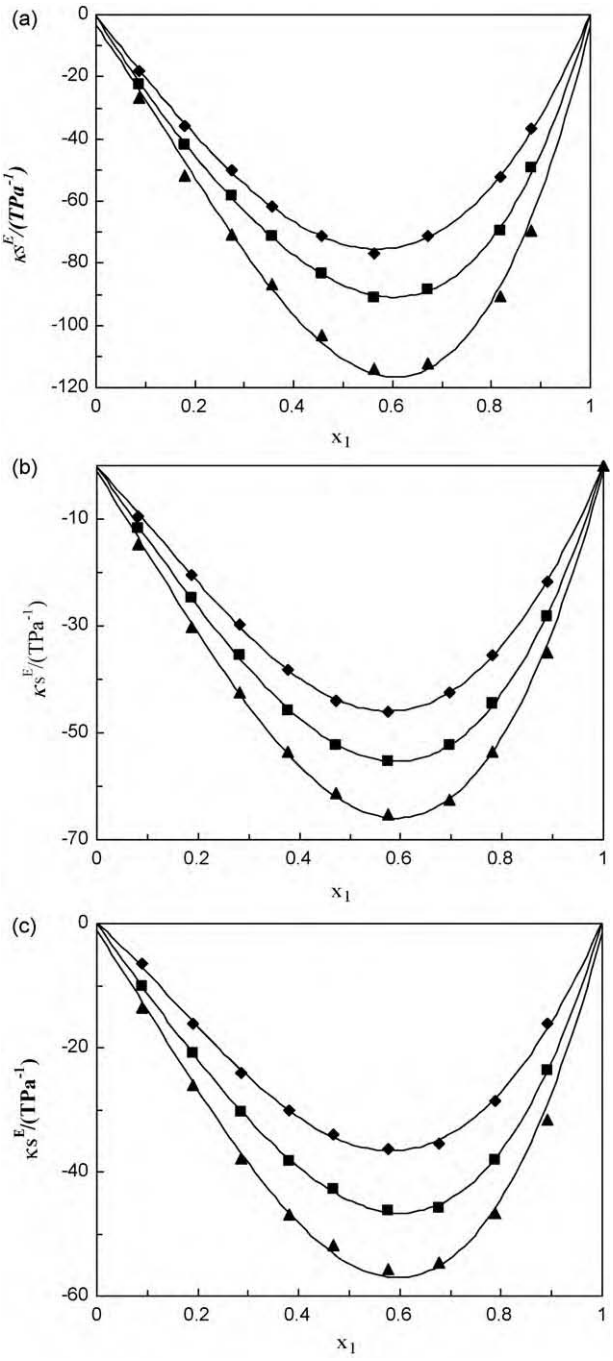

Fig. 2. Dependence of excess isentropic compressibilities on mole fraction of oxolane, (a) oxolane + aniline, (b) oxolane + N-methylaniline and (c) oxolane + N-ethylaniline at T = 303.15 K (●),303.15 K (■), and 323.15 K (▲).

association in oxolane and anilines, and (iii) aniline–oxolane cross-association and dipole–dipole interactions. The negative values of V_m^E and κ_S^E suggest qualitatively that dipole–dipole interactions (μ for oxolane = 1.75 D and for anilines ≈1.51 D [38]) and cross-association between aniline and oxolane components dominate over the dispersive ether–ether interactions, breaking of dipolar order of aniline as well as of oxolane and the disruption of H-bonding in primary (aniline) and secondary amines (N-methyl and N-ethylanilines). In the cross-association the H-atom of the aniline and substituted anilines interact with O-atom of the oxolane molecules. The negative κ_S^E and V_m^E values at equimolar concentrations follow the order aniline > N-ethylaniline > N-methylaniline. Apparently, from the values of excess functions, one can say that the strength of specific interactions between unlike molecules varies in the order aniline > N-methylaniline > N-ethylaniline. The decreased interactions from aniline to N-substituted aniline are caused by steric hindrance due to alkyl group attached to N-atom and strength of base. This observation is in accordance with the findings of Fort and Moore [45]. The decrease in the magnitude of negative κ_S^E and V_m^E with the rise in temperature further suggests that interactions between unlike components tend to reduce due to the increase in thermal motions.

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 oxolane (1) + N-methylaniline (2) mixture at 303.15, 313.15 and 323.15 K.

x_1	ρ (kg m^{-3})	u (m s^{-1})	κ_S (T Pa^{-1})	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 (T Pa^{-1})
303.15 K								
0.0000	978.2	1548	427	1267	1515	4.101		
0.0831	973.1	1528	440	1234	1487	4.167	−0.150	−9
0.1864	966.0	1502	459	1193	1451	4.254	−0.283	−20
0.2813	959.1	1478	477	1156	1418	4.339	−0.407	−30
0.3782	951.5	1453	498	1118	1383	4.430	−0.519	−38
0.4714	943.5	1428	520	1082	1347	4.529	−0.590	−44
0.5746	933.2	1396	550	1042	1303	4.657	−0.583	−46
0.6956	919.4	1357	591	997	1248	4.826	−0.488	−43
0.7823	908.2	1329	624	965	1207	4.960	−0.347	−36
0.8882	893.4	1293	669	927	1155	5.138	−0.155	−22
1.0000	877.3	1256	723	887	1102	5.339		
313.15 K								
0.0000	969.8	1512	451	1268	1467	4.290		
0.0831	964.9	1493	465	1235	1440	4.358	−0.179	−12
0.1864	958.3	1466	485	1193	1405	4.452	−0.389	−25
0.2813	951.4	1442	506	1155	1372	4.544	−0.538	−36
0.3782	944.0	1416	528	1117	1337	4.643	−0.677	−46
0.4714	936.0	1390	553	1081	1301	4.753	−0.767	−52
0.5746	926.0	1358	586	1041	1257	4.891	−0.806	−55
0.6956	912.2	1318	631	995	1202	5.075	−0.727	−52
0.7823	900.8	1289	669	963	1161	5.224	−0.582	−45
0.8882	885.7	1252	721	925	1109	5.425	−0.365	−28
1.0000	867.2	1212	785	886	1051	5.663		
323.15 K								
0.0000	961.0	1477	477	1270	1420	4.495		
0.0831	956.6	1459	491	1236	1396	4.562	−0.263	−15
0.1864	949.9	1433	513	1194	1361	4.661	−0.482	−30
0.2813	943.4	1407	535	1156	1328	4.762	−0.684	−43
0.3782	935.8	1381	560	1117	1292	4.873	−0.829	−54
0.4714	927.4	1354	588	1081	1256	4.993	−0.897	−61
0.5746	916.9	1322	624	1042	1212	5.143	−0.903	−65
0.6956	902.6	1282	674	996	1157	5.344	−0.792	−63
0.7823	891.1	1252	716	964	1115	5.510	−0.644	−54
0.8882	875.8	1213	776	926	1063	5.733	−0.426	−35
1.0000	856.6	1171	852	887	1003	6.007		

As expected, the trend of negative L_f^E values (Fig. 3 at 303.15 K) is similar to κ_S^E in all the systems. The negative values of L_f^E are generally observed in systems with specific interactions between unlike molecules. Fig. 4 shows that Z^E is positive for all the systems. 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 strong interactions between the unlike molecules. Positive trends in Z^E have also been reported for binary mixtures of methanol + piperidine [46].

The dependence of Rao's molar sound functions R on mole fractions x_1 is shown in Fig. 5. The Rao's molar sound functions R decrease with mole fraction of oxolane and are independent of temperature (Tables 2–4). The plots show that there are slight negative deviations from the linear dependence on x_1 for all three binary mixtures at all temperatures. According to Rao's approach [41], the

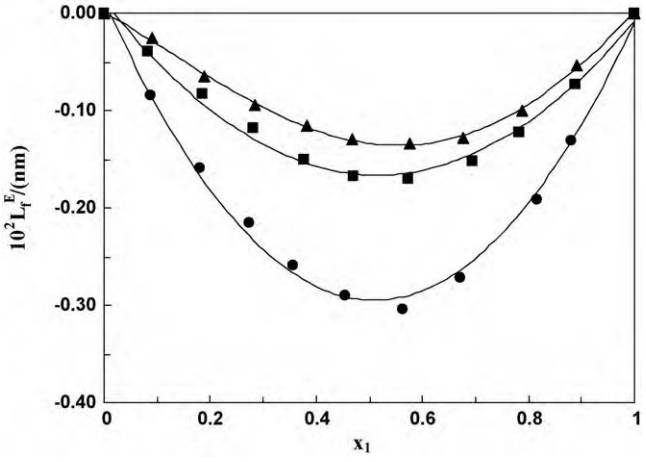

Fig. 3. Dependence of excess intermolecular free length on mole fraction of oxolane at T = 303.15 K (a) oxolane + aniline (●), (b) oxolane + N-methylaniline (■) and (c) oxolane + N-ethylaniline (▲).

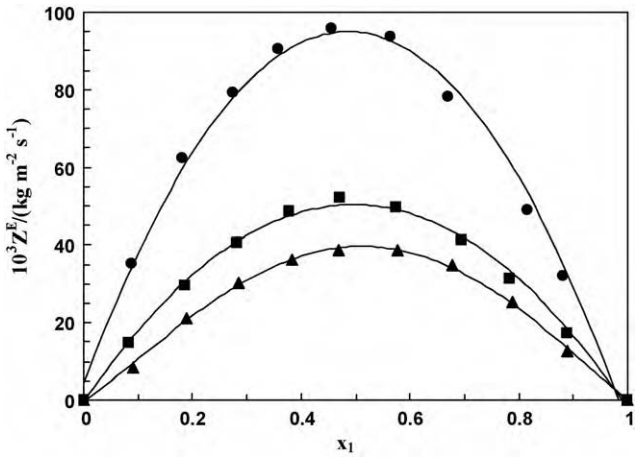

Fig. 4. Dependence of excess specific acoustic impedance on mole fraction of oxolane at T = 303.15 K (a) oxolane + aniline (●), (b) oxolane + N-methylaniline (■) and (c) oxolane + N-ethylaniline (▲).

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 (1) + N-ethylaniline (2) 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	$10^3 Z$ (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	951.9	1497	469	1456	1425	4.299		
0.0904	947.8	1482	480	1404	1405	4.351	−0.058	−7
0.1892	943.8	1469	491	1348	1386	4.401	−0.206	−16
0.2849	939.5	1452	505	1292	1365	4.461	−0.346	−24
0.3819	934.5	1433	521	1236	1339	4.534	−0.461	−30
0.4674	929.3	1414	538	1187	1314	4.607	−0.499	−34
0.5758	921.9	1387	564	1124	1279	4.715	−0.528	−36
0.6778	913.1	1360	592	1067	1242	4.833	−0.440	−36
0.7876	902.1	1326	630	1005	1196	4.985	−0.282	−29
0.8903	890.8	1291	673	947	1150	5.152	−0.152	−16
1.0000	877.3	1256	723	887	1102	5.339		
313.15 K								
0.0000	944.3	1462	495	1457	1381	4.497		
0.0904	940.8	1450	506	1404	1364	4.544	−0.163	−10
0.1892	936.7	1435	519	1347	1344	4.602	−0.330	−21
0.2849	932.4	1418	533	1292	1322	4.666	−0.494	−30
0.3819	927.6	1399	551	1235	1298	4.743	−0.648	−38
0.4674	922.6	1379	570	1185	1272	4.825	−0.723	−43
0.5758	915.2	1351	599	1123	1237	4.943	−0.779	−46
0.6778	906.4	1323	631	1065	1199	5.074	−0.711	−46
0.7876	895.4	1287	674	1003	1153	5.246	−0.576	−38
0.8903	882.8	1251	723	946	1105	5.435	−0.327	−24
1.0000	867.2	1212	785	886	1051	5.663		
323.15 K								
0.0000	935.9	1431	522	1459	1339	4.704		
0.0904	932.8	1420	532	1407	1324	4.747	−0.227	−14
0.1892	929.1	1404	546	1349	1305	4.810	−0.469	−26
0.2849	925.2	1388	561	1292	1284	4.877	−0.693	−38
0.3819	920.6	1367	581	1235	1259	4.963	−0.886	−47
0.4674	915.7	1346	603	1184	1232	5.056	−0.995	−52
0.5758	908.1	1317	635	1122	1196	5.189	−1.039	−56
0.6778	899.5	1286	672	1063	1157	5.337	−1.003	−55
0.7876	887.7	1250	721	1002	1110	5.526	−0.789	−47
0.8903	874.2	1215	775	946	1062	5.732	−0.460	−32
1.0000	857.1	1171	851	887	1004	6.005		

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 [47].

4. Estimation of speed of sound

The speed of sound u from the Nomoto's relation [17], Van Dael and Vangeel [18], Junjie's relation [19], impedance relation [20], collision factor theory [21,22], intermolecular free length theory [23], and Prigogine–Flory–Patterson–Oswal theory [24–27] have

Table 5
Coefficients A_i of Eq. (10) along with standard deviations σ of binary mixture properties.

Properties	Temperature	A_0	A_1	A_2	A_3		σ (Y^E)
Oxolane (1) + aniline (2)							
u (m s^{-1})	303.15	1615.4	−278.3	4.9	−189.9	103.7	1.1
	313.15	1584.0	−289.8	−35.3	−47.4		1.5
	323.15	1558.8	−246.9	−205.1	203.8	−139.8	1.5
κ_S (TPa^{-1})	303.15	378.5	165.7	45.6	133.4		0.9
	313.15	396.8	166.4	175.6	−144.5	191.6	1.0
	323.15	412.4	142.2	359.1	−490.3	427.8	1.0
Oxolane (1) + N-methylaniline (2)							
u (m s^{-1})	303.15	1548.4	−258.4	101.9	−279.5	143.6	0.4
	313.15	1511.9	−225.8	−76.0	1.0		0.8
	323.15	1477.6	−225.1	−78.7	−3.1		0.4
κ_S (TPa^{-1})	303.15	427.0	153.2	59.0	84.2		0.8
	313.15	450.7	174.4	32.7	127.6		0.3
	323.15	476.0	189.9	25.1	160.0		0.7
Oxolane (1) + N-ethylaniline (2)							
u (m s^{-1})	303.15	1497.1	−152.1	38.4	−253.0	125.4	0.8
	313.15	1461.8	−115.5	−130.7	−4.4		0.6
	323.15	1430.6	−106.6	−164.8	12.2		0.6
κ_S (TPa^{-1})	303.15	469.2	104.0	43.2	107.1		0.8
	313.15	495.1	116.5	20.0	153.7		0.4
	323.15	522.4	82.5	219.6	−130.1	156.2	0.7

Table 6
Coefficients B_i of Eq. (11) along with standard deviations $\sigma(Y^E)$ of excess properties of binary mixtures.

Properties	T (K)	B_0	B_1	B_2	B_3	$\sigma(Y^E)$
Oxolane (1) + aniline (2)						
$10^6 V_m^E$ (m^3 mol^{-1})	303.15	−3.583	−1.679	1.195	2.181	0.014
	313.15	−4.588	−2.025	−0.781	0.872	0.016
	323.15	−5.505	−4.02	−2.611	1.906	0.037
κ_S^E (T Pa^{-1})	303.15	−295.5	−97.5	3.4	32.4	0.7
	313.15	−349.1	−158.7	−52.3	54.2	0.8
	323.15	−429.7	−208.0	−119.2		1.1
$10^3 Z^E$ (kg m^{-2} s^{-1})	303.15	375.2	−77.6			1.8
$10^2 L_f^E$ (nm)	303.15	−1.175	−0.146			0.005
Oxolane (1) + N-methylaniline (2)						
$10^6 V_m^E$ (m^3 mol^{-1})	303.15	−2.327	−0.509	1.032	1.254	0.009
	313.15	−3.109	−0.806	0.15		0.012
	323.15	−3.548	−0.52	−0.361		0.023
κ_S^E (T Pa^{-1})	303.15	−178.1	−60.3	9.8		0.4
	313.15	−212.7	−83.3	−11.9		0.4
	323.15	−249.6	−100.3	−37.6		0.4
$10^3 Z^E$ (kg m^{-2} s^{-1})	303.15	205.5	−13.2	−37.6		0.5
$10^2 L_f^E$ (nm)	303.15	−0.652	−0.144			0.004
Oxolane (1) + N-ethylaniline (2)						
$10^6 V_m^E$ (m^3 mol^{-1})	303.15	−2.095	−0.371	1.511		0.014
	313.15	−2.996	−1.17	0.519	0.498	0.010
	323.15	−4.105	−1.509	0.555	0.448	0.009
κ_S^E (T Pa^{-1})	303.15	−143.7	−53.8	26.1		0.8
	313.15	−178.9	−75.3	−9.6		0.4
	323.15	−213.4	−80.9	−49.7	−33.6	0.5
$10^3 Z^E$ (kg m^{-2} s^{-1})	303.15	165.8	12.0	−61.7		1.0
$10^2 L_f^E$ (nm)	303.15	−0.516	−0.154			0.006

also been estimated for the present binary mixtures. The pertinent relations in these calculations and their theoretical basis have been outlined several times and will not be repeated here.

The speeds of sound u_{est} in the binary mixture over the entire range of composition were estimated. The standard percentage deviation σ% was calculated by considering dev% for all mole fractions using the relation

$$\sigma\% = \left[\frac{\Sigma(dev\%)^2}{n-1}\right]^{1/2} \quad (12)$$

where n represents number of data points.

The study of Table 7 reveals that the values of σ% for the NR, VVR, JR, IR, CFT, FLT, and PFPOT are in the range from 0.1 to 2.1, 5.1 to 8.0, 1.4 to 5.1, 0.4 to 1.9, 0.4 to 1.8, 1.2 to 2.8 and 1.0 to 3.3, respectively for the three binary mixtures at three temperatures investigated. The average values of standard deviations $\langle\sigma\%\rangle$ for the NR, IR and CFT are comparatively less than those found for other estimations.

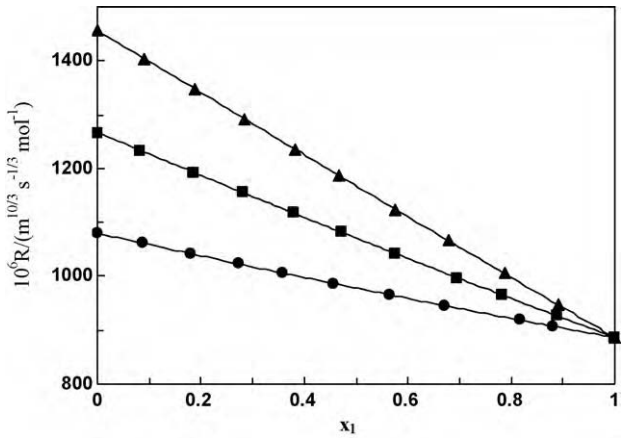

Fig. 5. Dependence of Rao's molar sound function on mole fraction of oxolane at T = 303.15 K (a) oxolane + aniline (●), (b) oxolane + N-methylaniline (■) and (c) oxolane + N-ethylaniline (▲).

Table 7
Standard percentage deviation (σ%) between experimental and estimated speed of sound using empirical or theoretical relations for binary mixtures.

T (K)	NR	VVR	JR	IR	CFT	FLT	PFPOT
Oxolane + aniline							
303.15 K	1.2	5.1	3.6	0.6	0.6	1.7	2.2
313.15 K	1.5	5.6	4.1	0.8	0.6	1.6	3.1
323.15 K	2.1	6.6	5.1	1.3	1.5	2.8	3.3
Oxolane + N-methylaniline							
303.15 K	0.1	5.3	1.6	0.4	0.4	1.2	1.6
313.15 K	0.1	5.7	1.9	0.6	0.6	1.2	2.3
323.15 K	0.3	6.1	2.3	0.7	0.8	1.5	2.5
Oxolane + N-ethylaniline							
303.15 K	0.4	6.9	1.4	1.4	1.2	1.3	1
313.15 K	0.6	7.5	1.8	1.7	1.5	1.6	1.7
323.15 K	0.8	8	2.2	1.9	1.8	2	3.6

Thus, the average values of standard deviation, the estimation ability of speed of sound in the presently investigated mixtures follows the sequence CFT ≅ NR > IR > FLT > PFPOT > JR > VVD.

5. Conclusions

The values of V_m^E, κ_S^E and L_f^E are negative and Z^E are positive for binary mixtures of oxolane with aniline, N-methylaniline and N-ethylaniline at 303.15, 313.15, and 323.15 K. There exist specific interactions between unlike molecules through hydrogen bonding and dipole–dipole interactions between unlike molecules. The estimation ability of speed of sound in the presently investigated mixtures follows the sequence CFT ≅ NR > IR > FLT > PFPOT > JR > VVD.

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