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Thermodynamic and Acoustic Properties of Binary Mixtures of Ethers. 2. Diisopropyl Ether with Arylamines at (303.15, 313.15, and 323.15) K and Application of ERAS Model to Aniline Mixtures with Diisopropyl Ether and Oxolane

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Densities, ρ, and speeds of sound, u, of binary mixtures formed by aniline or *N*-methylaniline or *N*-ethylaniline with diisopropyl ether (DIPE) 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, excess molar volumes, V_m^E, and excess isentropic compressibilities κ_S^E. The results have been used to investigate molecular interactions and structural effects in these mixtures. The speed of sound u in present mixtures has been estimated using several theoretical models to determine their relative predicting ability in terms of pure component properties. The ERAS model is applied to study V_m^E for DIPE−aniline and oxolane−aniline mixtures at (303.15, 313.15, and 323.15) K. The ERAS model represents qualitatively very large negative V_m^E data.

Introduction

The thermodynamic, acoustic, and transport properties of nonelectrolyte 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 behavior 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 anilines show very interesting features.[6] Systems with alkanols are characterized by quite large positive deviations from Raoult's law,[7,8] while linear amines + alkanol mixtures behave quite differently.[9] It has been reported that ethers interact with amines in their mixtures. Different volumetric and thermal effects are observed upon mixing because of the molecular interactions between ethers and amine.[10−13] 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 ether molecule. The aniline is predominantly used[14] as parent substance in the manufacture of several chemical products and intermediates. It is also used in the production of synthetic dyes and pigmennts, hydroquinone, drugs and agriculture chemicals, and as an accelerator in vulcanization of rubber. It is also used as a solvent and has been used as an antiknock compound for gasolines. Secondary amines *N*-methylaniline and *N*-ethylaniline are used as a latent and coupling solvent. It is well-known that oxolane is an excellent solvent of polymers, whereas diisopropyl ether is used as an oxygenate gasoline additive.[15,16] All this makes the study of ether-aromatic amine very interesting both industrially and theoretically. The systems, so chosen, provide us an opportunity for studying the effect of replacement of aminic hydrogen of aniline by methyl or ethyl group successively on the thermodynamic and acoustic properties of these systems. In the previous paper[17] we reported speeds of sound, isentropic compressibilities, Rao's molar sound functions, intermolecular free lengths, specific acoustic impedances, and various calculated excess properties of three binary mixtures of oxolane with aniline, *N*-methylaniline, and *N*-ethylaniline at (303.15, 313.15, and 323.15) K. It was found that dipole−dipole interactions and cross-association between anilines and oxolane components dominate over the dispersive ether−ether interactions and breaking of dipolar order of both the components and the disruption of H-bonding anilines. In this paper, we extend the work on mixtures of diisopropyl ether with same aromatic amines, in order to find the effect of replacing oxolane (cyclic ether) with diisopropyl ether (open chain ether) with larger free volume on the properties and molecular interactions. Recently, Khammar and Shaw[18] described and tested several predictive methods for speed of sound in alkanol + *n*-alkanes mixtures. There is a large and growing database for speed of sound values for pure constituents, for high precision applications, one approach is to use measured speed of sound values in pure components directly, and to make use of mixing rules, association equilibrium models, or equations of state to estimate mixture effects as accurately as possible. This is the preferred approach in the literature. Here, we have examined Schaaffs' collision factor theory (CFT),[19,20] Jacobson's free length theory (FLT),[21] and Prigogine−Flory−Patterson−Oswal theory (PFPOT)[22−25] to estimate speeds of sound in investigated binary mixtures at different temperatures. The V_m^E results for DIPE−aniline and oxolane−aniline[17] are also analyzed in terms of ERAS model.[26,27]

Experimental Section

Materials. 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

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Table 1. Densities (ρ), Speeds of Sound (u), Thermal Expansion Coefficients (α), and Heat Capacities (C_P) for Pure Liquids

	T	ρ		u		α^{oa}	C_P^o
		$kg \cdot m^{-3}$		$m \cdot s^{-1}$			
liquid	K	exp.	lit.	exp.	lit.	kK^{-1}	$J \cdot mol^{-1} \cdot K^{-1}$
DIPE	303.15	713.3	713.1[b] 713.5[d] 713.06[g]	975	974.9[c] 976.04[f]	1.468	217[d,e]
	313.15	702.9	702.80[b]	934	932.17[f]	1.489	219[d,e]
	323.15	692.3	691.53[f]	892	888.61[f]	1.512	221[d,e]
aniline	303.15	1012.9	1012.9[h] 1012.8[i] 1013.04[k]	1615	1614.5[j] 1619[m] 1619.2[k]	0.851	191[d,e]
	313.15	1004.9	1004.4[i] 1004.6[l]	1582	1579.5[m] 1581.4[k]	0.858	194[d,e]
	323.15	996.9	995.89 996.6[n]	1550		0.866	197[d,e]
N-methyl aniline	303.15	978.2	977.71[l] 978.1[i] 978.01[k]	1548	1545.5[k]	0.816	211[d,e]
	313.15	969.8	969.9[i] 969.6[l]	1512		0.822	214[d,e]
	323.15	961.5	961.9[i]	1477		0.830	218[d,e]
N-ethyl aniline	303.15	952.6	952.6[l]	1497		0.885	227[d,e]
	313.15	944.2	944.2[l]	1462		0.893	230[d,e]
	323.15	935.9		1431		0.902	233[d,e]

[a] Derived from density data from refs 28−32. [b] Reference 28. [c] Reference 32. [d] Reference 29. [e] Estimated from group contribution method of Chueh-Swanson and Missenard.[43] [f] Reference 33. [g] Reference 34. [h] Reference 35. [i] Reference 30. [j] Reference 36. [k] Reference 37. [l] Reference 31. [m] Reference 38. [n] Reference 39.

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 velocities with those reported in the literature. The measured values are included in Table 1 along with the available literature values.[28−39]

Apparatus and Procedure. 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 accuracy within ± 0.02 K. The details of the experimental procedure have been described elsewhere.[40] The binary mixtures were prepared by mixing known masses of pure liquids in airtight 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 measurement were immediately used after preparation. The uncertainty in density and speed of sound measurements was within 0.1 $kg \cdot m^{-3}$ and 1 $m \cdot s^{-1}$.

Results and Discussion

The results for the densities, speeds of sound, isentropic compressibilities, excess molar volumes, and excess isentropic compressibilities for mixtures of DIPE with aniline, *N*-methylaniline, and *N*-ethylaniline at (303.15, 313.15, and 323.15) K are given in Tables 2 to 4.

From the values of densities and speeds of sound, the isentropic compressibilities were obtained using the Laplace relation

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

Table 2. Densities (ρ), Speeds of Sound (u), Isentropic Compressibilities (κ_S), Excess Molar Volumes (V_m^E) and Excess Isentropic Compressibilities (κ_S^E) for DIPE + Aniline Mixture at (303.15, 313.15, and 323.15) K

	ρ	u	κ_S	$10^6 V_m^E$	κ_S^E
x_1	$kg \cdot m^{-3}$	$m \cdot s^{-1}$	TPa^{-1}	$m^3 \cdot mol^{-1}$	TPa^{-1}
			303.15 K		
0.0000	1012.9	1615	379		
0.0707	988.8	1555	419	−0.739	−90
0.1488	962.3	1492	467	−1.400	−172
0.2307	935.0	1431	522	−1.943	−239
0.3178	907.0	1368	589	−2.399	−290
0.4169	875.8	1301	675	−2.688	−323
0.5201	844.2	1234	777	−2.735	−330
0.6208	814.1	1175	890	−2.497	−312
0.7396	779.7	1108	1045	−1.862	−256
0.8673	744.9	1041	1239	−0.881	−153
1.0000	713.3	975	1475		
			313.15 K		
0.0000	1004.9	1581	398		
0.0707	981.6	1526	438	−0.874	−107
0.1488	955.8	1465	488	−1.671	−204
0.2307	929.1	1401	548	−2.348	−282
0.3178	901.3	1338	620	−2.902	−342
0.4169	870.3	1268	715	−3.299	−381
0.5201	838.7	1203	824	−3.428	−395
0.6208	808.5	1142	949	−3.250	−377
0.7396	773.8	1075	1118	−2.644	−317
0.8673	737.8	1005	1341	−1.512	−198
1.0000	702.9	934	1631		
			323.15 K		
0.0000	996.9	1548	419		
0.0707	974.3	1497	458	−1.006	−128
0.1488	949.4	1437	510	−1.969	−243
0.2307	923.2	1372	575	−2.779	−335
0.3178	895.8	1306	655	−3.463	−406
0.4169	864.8	1236	757	−3.953	−456
0.5201	833.1	1169	878	−4.159	−474
0.6208	802.9	1108	1015	−4.062	−459
0.7396	767.9	1041	1202	−3.492	−396
0.8673	730.8	970	1454	−2.230	−261
1.0000	692.3	891	1820		

The values of κ_S are uncertain within ± 0.2 %.

Excess molar volume and excess isentropic compressibility in each mixture were calculated with the following expressions:

$$Y^E = Y - Y^{id} \tag{2}$$

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

$$V_m^{id} = \sum x_i V_i^o = \sum x_i M_i / \rho_i \tag{3}$$

In which x_i, V_i^o, and M_i are the mole fraction, molar volume, and molar mass of component i. $\kappa_S{}^{id}$ for an ideal mixture was calculated from the relation recommended by Benson and Kiyohara[41] and Douheret et al.[42]

$$\kappa_s^{id} = \sum \phi_i \{\kappa_{S,i}^o + TV_i^o(\alpha_i^o)^2 / C_{p,i}^o\} - T(\sum x_i V_i^o)(\sum \phi_i \alpha_i^{o2} / (\sum x_i C_i^o)) \tag{4}$$

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, $\phi_i = x_i V_i / \sum x_j V_j$ is the volume fraction of i in the mixture, stated in terms of the unmixed

Table 3. Densities (ρ), Speeds of Sound (u), Isentropic Compressibilities (κ_S), Excess Molar Volumes (V_m^E), and Excess Isentropic Compressibilities (κ_S^E) for DIPE + *N*-Methylaniline Mixture at (303.15, 313.15, and 323.15) K

x_1	ρ / $kg\cdot m^{-3}$	u / $m\cdot s^{-1}$	κ_S / TPa^{-1}	$10^6 V_m^E$ / $m^3\cdot mol^{-1}$	κ_S^E / TPa^{-1}
		303.15 K			
0.0000	978.2	1548	427		
0.0742	958.3	1501	463	−0.611	−75
0.1544	936.8	1449	508	−1.183	−143
0.2393	914.0	1395	562	−1.674	−200
0.3269	890.6	1342	624	−2.070	−246
0.4266	864.1	1282	704	−2.370	−278
0.5274	837.3	1224	797	−2.476	−290
0.6283	810.5	1169	903	−2.369	−280
0.7442	779.8	1107	1047	−1.962	−237
0.8661	747.7	1041	1234	−1.186	−147
1.0000	713.3	975	1475		
		313.15 K			
0.0000	969.8	1512	451		
0.0742	951.4	1465	490	−0.839	−87
0.1544	930.5	1414	538	−1.544	−166
0.2393	907.9	1360	596	−2.124	−234
0.3269	884.5	1307	662	−2.584	−288
0.4266	857.8	1248	749	−2.926	−328
0.5274	831.0	1190	850	−3.096	−345
0.6283	804.2	1134	967	−3.047	−336
0.7442	773.2	1072	1126	−2.649	−290
0.8661	740.1	1007	1332	−1.736	−193
1.0000	702.9	934	1631		
		323.15 K			
0.0000	961.5	1477	477		
0.0742	944.6	1430	518	−1.079	−102
0.1544	924.4	1379	569	−1.939	−195
0.2393	901.9	1326	631	−2.606	−277
0.3269	878.3	1273	703	−3.111	−342
0.4266	851.4	1214	797	−3.502	−391
0.5274	824.5	1156	907	−3.729	−415
0.6283	797.7	1099	1038	−3.746	−406
0.7442	766.6	1035	1218	−3.398	−355
0.8661	732.5	966	1462	−2.350	−233
1.0000	692.3	892	1815		

Table 4. Densities (ρ), Speeds of Sound (u), Isentropic Compressibilities (κ_S), Excess Molar Volumes (V_m^E) and Excess Isentropic Compressibilities (κ_S^E) for DIPE + *N*-Ethylaniline Mixture at (303.15, 313.15, and 323.15) K

x_1	ρ / $kg\cdot m^{-3}$	u / $m\cdot s^{-1}$	κ_S / TPa^{-1}	$10^6 V_m^E$ / $m^3\cdot mol^{-1}$	κ_S^E / TPa^{-1}
		303.15 K			
0.0000	952.6	1497	468		
0.0735	936.7	1459	502	−0.510	−57
0.1577	917.9	1417	543	−0.985	−116
0.2410	899.3	1372	591	−1.417	−163
0.3228	880.9	1329	643	−1.786	−202
0.4216	858.5	1275	716	−2.149	−233
0.5267	833.9	1219	807	−2.341	−249
0.6288	809.0	1167	908	−2.273	−246
0.7478	778.7	1105	1051	−1.832	−212
0.8697	746.7	1043	1230	−1.002	−139
1.0000	713.3	975	1475		
		313.15 K			
0.0000	944.2	1462	496		
0.0735	929.0	1425	530	−0.655	−68
0.1577	910.9	1382	575	−1.283	−136
0.2410	892.5	1340	624	−1.799	−194
0.3228	874.1	1296	681	−2.220	−240
0.4216	851.5	1243	760	−2.614	−280
0.5267	826.7	1187	859	−2.832	−301
0.6288	801.7	1132	973	−2.796	−297
0.7478	771.3	1068	1136	−2.384	−257
0.8697	738.7	1004	1342	−1.475	−170
1.0000	702.9	934	1631		
		323.15 K			
0.0000	935.9	1431	522		
0.0735	921.2	1391	561	−0.781	−78
0.1577	903.7	1346	610	−1.559	−158
0.2410	885.7	1301	668	−2.197	−224
0.3228	867.4	1258	729	−2.693	−279
0.4216	844.6	1205	816	−3.125	−327
0.5267	819.5	1149	925	−3.361	−355
0.6288	794.4	1094	1052	−3.366	−353
0.7478	763.9	1030	1233	−2.992	−312
0.8697	730.8	963	1476	−2.027	−204
1.0000	692.3	892	1815		

components and $\rho^{id} = \sum \phi_i \rho_i^o$. The values of α^o and C_P^o[29], 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

$$u \quad \text{or} \quad \kappa_S \sum_{i=1}^{m} A_i x_1^{i-1} \tag{5}$$

The V_m^E and κ_S^E were correlated by Redlich−Kister polynomial equation

$$V_m^E \quad \text{or} \quad \kappa_S^E = x_1(1 - x_1) \sum_{i}^{n} B_i (1 - 2x_1)^i \tag{6}$$

The coefficients A_i of eq 5 and B_i of eq 6 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 to 4 that the values of speeds of sound decrease with mole fraction of DIPE and also with the rise in temperature for all the mixtures studied, while opposite is the case with the values of isentropic compressibility. Figures 1 and 2 show the dependence of V_m^E and κ_S^E on composition. The V_m^E and κ_S^E are very large and negative for all the three investigated mixtures over the entire mole fraction range, and their magnitude increases with the rise in temperature from (303.15 to 323.15) K. The minima in V_m^E and κ_S^E occur around 0.55 mol fraction in the studied mixtures.

The observed values of V_m^E for presently investigated mixtures are some of the largest negative values found for organic mixtures in the literature. Other very large negative values of V_m^E reported include alkanol + TEA (-2.23 to -1.92×10^{-6} $m^3\cdot mol^{-1}$),[44] 2-methoxyethanol + tert-butylamine (-2.4 to -2.6×10^{-6} $m^3\cdot mol^{-1}$),[45] and DMSO + cyclohexylamine (-3.4×10^{-6} $m^3\cdot mol^{-1}$).[46]

The over all behavior 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 DIPE and aryl amines, (iii) aryl amine-DIPE cross association and dipole−dipole interactions, (iv) free volume effect, and (v) characteristic pressure P^* effect.[47,48] The estimated sum of free volume and characteristic pressure contributions to the total V_m^E as per the Prigogine−Flory−Patterson (PFP) theory[22−24] is in the range from -2.27 to -2.73×10^{-6} $m^3\cdot mol^{-1}$ for DIPE + aniline, from -2.16 to -2.58×10^{-6} $m^3\cdot mol^{-1}$ for DIPE + methylaniline, and from -1.90 to -2.30×10^{-6} $m^3\cdot mol^{-1}$ for DIPE + ethylaniline. Still larger negative values of V_m^E than these values for the present mixtures suggest that the dipole−dipole interactions (μ for DIPE = 1.34 D and for anilines ≈ 1.51 D[30]), and cross-association between aromatic amine and DIPE components dominate over the dispersive ether−ether interactions, breaking of dipolar order

Table 5. Coefficients A_i of eq 5 along with Standard Deviations σ of Binary Mixture Properties

properties	T/K	A_0	A_1	A_2	A_3	A_4	σ (Y^E)
				DIPE + Aniline			
u/m·s^{-1}	303.15	1614.6	−860.7	277.9	−45.3	−11.6	0.6
	313.15	1581.6	−796.1	−10.5	377.0	−218.2	1.1
	323.15	1548.6	−692.3	−386.0	829.3	−409.1	1.1
κ_S/TPa^{-1}	303.15	378.6	537.5	338.5	161.9	58.7	0.8
	313.15	398.3	500.6	735.0	−475.4	472.0	1.1
	323.15	419.4	435.7	1171.9	−1085.7	877.9	1.0
				DIPE + *N*-Methylaniline			
u/m·s^{-1}	303.15	1548.8	−668.0	108.4	−14.4		0.9
	313.15	1512.2	−638.7	−28.9	222.5	−133.1	0.3
	323.15	1477.8	−667.6	142.6	−61.1		0.8
κ_S/TPa^{-1}	303.15	426.1	483.9	332.0	68.0	165.5	1.3
	313.15	451.7	450.4	753.3	−674.7	649.4	1.4
	323.15	476.6	504.2	699.7	−595.5	730.5	0.5
				DIPE + *N*-Ethylaniline			
u/m·s^{-1}	303.15	1496.6	−486.8	−182.9	273.1	−124.8	0.5
	313.15	1462.0	−497.8	−63.0	33.2		0.6
	323.15	1430.9	−541.1	18.9	−16.9		0.5
κ_S/TPa^{-1}	303.15	469.0	392.6	513.4	−285.3	384.8	0.8
	313.15	496.1	414.1	538.1	−273.0	454.8	1.3
	323.15	522.3	472.7	593.3	−419.8	646.6	1.0

Table 6. Coefficients B_i of eq 6 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 + Aniline			
$10^6V_m^E$/m^3·mol^{-1}	303.15	−11.0142	−0.7338	3.0519	−2.9339	0.0066
	313.15	−13.7149	0.8113	0.9914	−1.5913	0.0046
	323.15	−16.5976	2.2747	−1.5365	0.7166	0.0065
κ_S^E/TPa^{-1}	303.15	−1324.7	−19.3	−441.5		0.6
	313.15	−1578.4	65.0	−150.3		0.6
	323.15	−1887.8	152.7	−380.2	140.6	0.9
			DIPE + *N*-Methylaniline			
$10^6V_m^E$/m^3·mol^{-1}	303.15	−9.8771	1.2405	0.4900	−0.7265	0.0036
	313.15	−12.2809	2.4794	−2.1659	−0.7437	0.0036
	323.15	−14.7465	3.7344	−5.4326	−0.3151	0.0034
κ_S^E/TPa^{-1}	303.15	−1161.9	156.5	−30.1	−71.1	1.5
	313.15	−1370.2	227.5	−176.8	61.5	0.5
	323.15	−1645.1	345.5	−193.4		0.5
			DIPE + *N*-Ethylaniline			
$10^6V_m^E$/m^3·mol^{-1}	303.15	−9.2495	2.7442	2.0377	−3.2804	0.0055
	313.15	−11.1922	3.1522	−0.2284	−1.5465	0.0032
	323.15	−13.2987	3.5507	−2.6880	1.2197	0.0022
κ_S^E/TPa^{-1}	303.15	−990.5	236.4	−82.5		1.1
	313.15	−1187.5	285.6	−118.3	60.0	0.7
	323.15	−1401.8	408.6	−157.7	42.7	0.4

of aromatic amines as well as of DIPE and the disruption of H-bonding in primary (aniline) and secondary aromatic amines (*N*-methyl and *N*-ethylanilines). In the cross-association, the H-atom of the present aromatic amines interacts with O-atom of the DIPE molecules. The negative V_m^E and κ_S^E values at equimolar compositions follow the order: aniline > *N*-methylaniline > *N*-ethylaniline. Apparently, from the values of excess functions, one can say that the strength of specific interactions between unlike components 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 the base.

Estimation of Speeds of Sound. The speed of sound from the Schaaffs' collision factor theory,[19,20] Jacobson's intermolecular free length theory,[21] and Prigogine−Flory−Patterson−Oswal statistical theory[22−25] have been estimated over the entire range of composition and at (303.15, 313.15, and 323.15) K for the studied binary mixtures. The pertinent relations in these calculations and their theoretical basis have been outlined several times[4,25] and will not be repeated here. In order to determine relative predicting ability of various models, the standard percentage deviation σ % was calculated by considering percentage deviations for all mole fractions using the relation (7) and recorded in Table 7.

$$\sigma\,\% = \left[\sum\left\{\frac{100(u_{\text{exp}} - u_{\text{cal}})}{u_{\text{expt}}}\right\}^2 \Big/ n\right]^{1/2} \tag{7}$$

where n represents number of data points.

The study of Table 7 reveals that the values of σ % for the CFT, FLT, and PFPOT are in the range from 1.1 to 4.7, 2.8 to 5.9, and 2.1 to 4.5 %, respectively for the three binary mixtures at investigated temperatures. The average values of standard deviations $\langle\sigma\,\%\rangle$ for the CFT, FLT, and PFPOT are 2.9, 3.9, and 3.2, respectively. Thus, the average values of standard

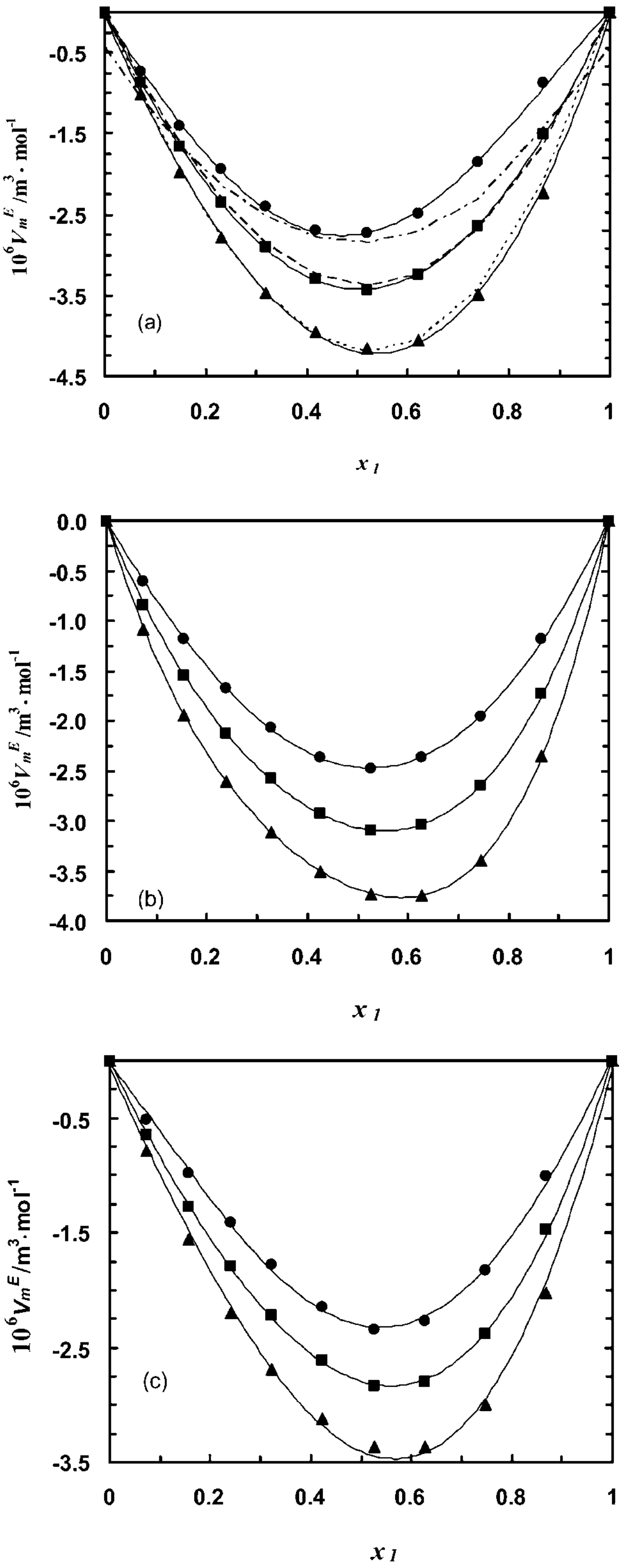

Figure 1. Dependence of excess molar volumes on mole fraction of DIPE, (a) DIPE + aniline, (b) DIPE + *N*-methylaniline and (c) DIPE + *N*-ethylaniline at $T =$ ●, 303.15 K; ■, 313.15 K; ▲, 323.15 K. Solid lines have been drawn from eq 6 using the coefficient given in Table 6. Dashed lines in (a) represent ERAS results.

deviation, the estimation ability of speed of sound in the presently investigated mixtures follows the sequence CFT > PFPOT > FLT. Thus for present mixtures CFT gives the best prediction while FLT least.

Application of ERAS Model to V_m^E. The present aryl amines are self-associated through hydrogen bonding. UNIQUAC associated solution model[49] has been applied by Nagata and co-workers[50,51] to correlate the excess thermodynamic properties of binary-ternary phase equilibria and excess enthalpies of aniline with hydrocarbons and alkanols. However, this model has a characteristic limitation to describe the volumetric and related properties of such systems as it assumes volume of mixing to be zero. This limitation was overcome by the two association models developed at the same time by Treszczanowicz and Benson[52] and by Heintz,[26] which combines the linear-chain association model[53,54] with Flory's equation of state.[23] Both the models are quite successful in describing volumetric properties of alkanol + alkane or cycloalkane mixtures.[26,52,55−58] The model due to Heintz[26] popularly known as extended real associated solution model (ERAS) applicable

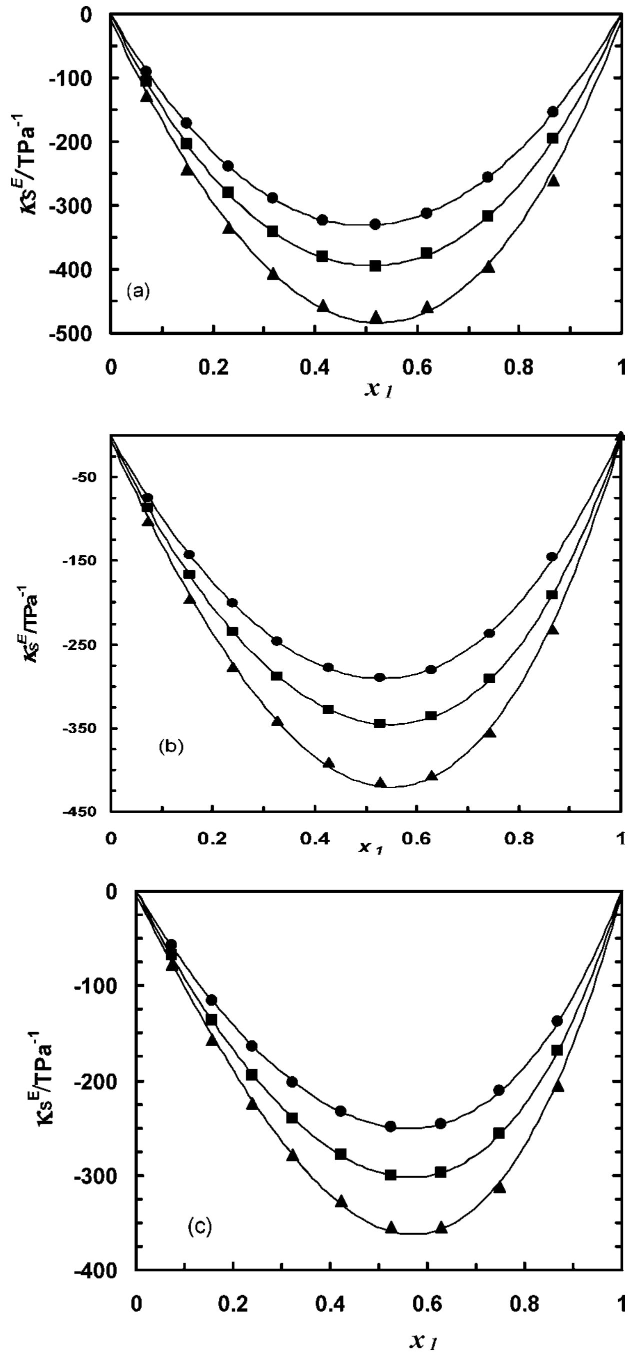

Figure 2. Dependence of excess isentropic compressibilities on mole fraction of DIPE, (a) DIPE + aniline, (b) DIPE + *N*-methylaniline, and (c) DIPE + *N*-ethylaniline at $T =$ ●, 303.15 K; ■, 313.15 K; ▲, 323.15 K. Solid lines have been drawn from eq 6 using coefficient given in Table 6.

Table 7. Standard Percentage Deviation (σ %) Between Experimental and Estimated Speed of Sound using Theoretical Relations for Binary Mixtures

T / K	CFT	FLT	PFPOT
	DIPE + Aniline		
303.15	4.6	3.6	3.3
313.15	4.7	4.3	3.2
323.15	4.7	5.9	4.5
	DIPE + *N*-Methylaniline		
303.15	2.6	2.8	2.7
313.15	2.7	3.9	3.1
323.15	2.9	5.4	3.7
	DIPE + *N*-Ethylaniline		
303.15	1.1	2.1	2.1
313.15	1.1	2.8	2.6
323.15	1.6	4.1	3.6

to alkanol + alkane has subsequently been extended[27] and successfully applied[59−63] to mixtures consisting of one strongly associating component (*A*, alkanol) and other weakly associating component (*B*, alkylamine). In addition, cross-association (A_iB or A_iB_j) in the mixture can also be accounted for. ERAS model has also been used to analyze the excess molar enthalpy H_m^E and excess molar volume V_m^E data of linear amine + ether systems.[64,65] To our knowledge, the applicability of the ERAS model to correlate thermodynamic properties of aniline mixtures with *n*-hexane, *n*-octane, methanol, ethanol, 1-propanol, and 1-butanol has been examined by Gonzalez et al.[6] Here we apply the ERAS model to correlate V_m^E of DIPE + aniline, oxolane + aniline (studied in earlier paper[17]) mixtures at (303.15, 313.15, and 323.15) K, since, the ERAS parameters for aniline, DIPE, and oxolane are available.[6,66,67] For methyl aniline and ethyl aniline, ERAS parameters specially association constant and enthalpy of H-bond formation are not available.

In the framework of ERAS model, self-association of associating component (A, aniline) and polar nonassociating (B, oxolane or DIPE) occurs, according to the following reaction scheme:

$$A_m + A \overset{K_A}{\longleftrightarrow} A_{m+1} \tag{8}$$

$$B_m + B \overset{K_B}{\longleftrightarrow} B_{n+1} \tag{9}$$

where *m* or *n* are the degree of self-association, ranging from 1 to ∞. The cross-association between *A* self-associated species and *B* (ether) molecules is represented by

$$A_m + B_n \overset{K_{AB}}{\longleftrightarrow} A_mB_n \tag{10}$$

The association constants K_i (i = A, B, and AB) are assumed to be independent of the chain length. Their temperature dependence is given by

$$K_i = K_0 \exp\left[-\left(\frac{\Delta h_i^*}{R}\right)\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{11}$$

where K_0 is the equilibrium constant at the standard temperature T_0 (298.15 K), R the gas constant and Δh_i^* the enthalpy for the reactions given by eqs 8 to 10, which corresponds to the hydrogen bonding energy. These reactions are also characterized by the volume change Δv_i^* related to the formation of the linear chains.

The excess functions are split into two additive terms, which arise from hydrogen-bonding effects (so-called chemical contribution) and nonpolar van der Waals' interactions including free volume effects (so-called physical contribution). The expressions for V_m^E of the ERAS model extended to the two block approach of cross-association are given by[27,62]

$$V_{\text{ERAS}}^E = V_{\text{phy}}^E + V_{\text{chem}}^E \tag{12}$$

$$V_{\text{phy}}^E = (x_A V_A^* + x_B V_B^*)(\tilde{V}_M - \phi_A \tilde{V}_A - \phi_B \tilde{V}_B) \tag{13}$$

$$V_{\text{chem}}^E = \tilde{V}_M \left\{ x_A K_A \Delta v_A^* (\phi_{A1} - \phi_{A1}^o) + x_B K_B \Delta v_B^* (\phi_{B1} - \phi_{B1}^o) + x_A K_{AB} \Delta v_{AB}^* \frac{\phi_{B1}(1 - K_A \phi_{A1})}{(V_B/V_A)(1 - K_B \phi_{B1}) + K_{AB}\phi_{B1}} \right\} \tag{14}$$

where K_{AB} and Δh_{AB}^* are the association constant and hydrogen bond energy for the cross-association. ϕ_{A1} and ϕ_{B1} are the hard core volume fractions of the component in the mixture.

The physical contribution in ERAS model is derived from Flory's equation of state,[23] which is assumed to be valid not only for pure components but also for the mixture.

$$\frac{\tilde{P}_i \tilde{V}_i}{\tilde{T}_i} = \frac{\tilde{V}_i^{1/3}}{\tilde{V}_i^{1/3} - 1} - \frac{1}{\tilde{V}_i \tilde{T}_i} \tag{15}$$

where i = A, B, and M (mixture). In eq 15 $\tilde{V}_i = V_{m,i}/V_i^*$; $\tilde{P}_i = P_{m,i}/P_i^*$; $\tilde{T}_i = T_{m,i}/T_i^*$; are the reduced volume, pressure and temperature, respectively. All of the reduction parameters of pure components can be determined knowing the experimental data for molar volume V_m, thermal expansion coefficient α, isothermal compressibility κ_T, provided suitable association parameters, K_i, Δh_i^*, and Δv_i^* are known. The reduction parameters for the mixtures P_M^*, T_M^*, and V_M^* are calculated from mixing rules.[26,65] Details are given elsewhere.[27,59]

ERAS Parameters. There is no self-association of DIPE and oxolane molecules that does occur in alkanols or primary or secondary amines through hydrogen bonding. DIPE molecules have been treated as nonassociated molecules in analysis of DIPE-heptane mixtures through ERAS model.[66] However, the mixtures oxolane + alkane[67] and oxolane-hetane-TEA[68] have been analyzed within the framework of the ERAS model, considering weak polar-association being present for oxolane. Weak self-association in these molecules was considered as being a formal result of the model calculations, rather than providing evidence that real association occurs in the latter molecules. It was interpreted as preferential interactions among oxolane molecules due to their dipole moments. Accordingly, as recommended, we have also treated oxolane as being a weak dipolar-associated molecule with K_i = 0.5, Δh_i^* = −8.0 kJ·mol^{-1}, and Δv_i^* = −1.7 cm^3·mol^{-1} at 298.15 K.[68] For self-associated aniline, the values of K = 14.8, Δh_i^* = −15.0 kJ·mol^{-1}, and Δv_i^* = −12.0 cm^3·mol^{-1} at 298.15 K were determined by Gonzalez et al.[6]

Table 8. Equilibrium Constant *K*, Isothermal Compressibility (κ_T/TPa^{-1}), Molar Volume (V_m/cm$^3\cdot$mol^{-1}), Reduction Parameter *V*/cm$^3\cdot$mol^{-1} and *P*/J$\cdot$cm^{-3}, Surface to Volume Ratio (*S*/nm^{-1}), and Enthalpy and Volume of Hydrogen Bonding Δh^*/kJ$\cdot$mol^{-1} and Δv^*/cm$^3\cdot$mol^{-1}

T / K	*K*	κ_T	V_m	V^*	P^*	S^a	Δh^*	Δv^*
				Aniline				
303.15	13.4^b	484^c	91.94	79.98	454	12.54	−15^d	−12^d
313.15	11.1^b	508^c	92.67	80.18	458	12.54	−15^d	−12^d
323.15	9.3^b	533^c	93.42	80.34	464	12.54	−15^d	−12^d
				Diisopropyl Ether				
303.15	0	1894^c	143.24	106.85	422	14.20	0	0
313.15	0	2091^c	145.36	107.45	408	14.20	0	0
323.15	0	2308^c	147.59	108.09	395	14.20	0	0
				Oxolane				
303.15	0.47^e	1035^c	82.19	63.61	590	13.31	−8^f	−1.7^f
313.15	0.43^e	1112^c	83.15	63.73	590	14.20	−8^f	−1.7^f
323.15	0.39^e	1194^c	84.18	63.90	590	14.20	−8^f	−1.7^f

[a] Calculated according to Bondi.[69] [b] Calculated using eq 11 and employing values of K_i and Δh^*Z at 298. Fifteen from ref 6. [c] Derived from κ_S, α, V_m, and C_P using equation $\kappa_T = \kappa_S + \alpha^2 V_m T/C_P$. [d] Reference 6. [e] Calculated using eq 11 and employing values of K_i and Δh^*Z at 298.15 from ref 68. [f] Reference 68.

Table 9. ERAS Parameters at Temperature *T* for DIPE + Aniline and Oxolane + Aniline

mixtures	*T* / K	X_{AB} / J$\cdot$cm^{-3}	K_{AB}	Δh^*_{AB}^{a} / kJ$\cdot$mol^{-1}	Δv^*_{AB} / cm$^3\cdot$mol^{-1}
DIPE + aniline	303.15	2.0	7.2	−11.7	−12.2
	313.15	2.0	6.2	−11.7	−13.8
	323.15	2.0	6.0	−11.7	−15.3
oxolane + aniline	303.15	2.8	7.1	−11.7	−13.6
	313.15	2.8	8.0	−11.7	−14.4
	323.15	2.8	8.0	−11.7	−15.4

[a] Derived from H^E_m of oxolane + propylamine considered equivalent to hydrogen bon energy for DIPE + aniline and oxolane + aniline.

The ERAS reduction parameters V^*_i, P^*_i, and T^*_i at (303.15, 313.15, and 323.15) K were then evaluated from α_i, $\kappa_{T,i}$, and $V_{m,i}$ at corresponding temperature, and association parameters K_i, Δh^*_i, and Δv^*_i. The Δh^*_i and Δv^*_i are independent of temperature, whereas K_i is consistent with eq 11. The ERAS parameters for aniline, oxolane, and DIPE at different temperatures are collected in Table 8. It should be mentioned that the values of surface to volume ratio S were estimated from group volumes and surfaces as recommended by Bondi.[69] The unknown parameters K_{AB}, Δh^*_{AB}, Δv^*_{AB}, and X_{AB} are normally obtained from a simultaneous adjustment to experimental data of V^E_m and H^E_m. In the absence of H^E_m data for presently investigated mixtures, we have taken cross-association hydrogen bond energy Δh^*_{AB} of DIPE-aniline and oxolane-aniline as −11.45 kJ$\cdot$mol^{-1}, equivalent to cross-association hydrogen bond energy Δh^*_{AB} for oxolane-propylamine.[13] The optimum values of unknown parameters K_{AB}, Δv^*_{AB}, and X_{AB} at required temperature were then obtained by adjusting whole composition range V^E_m, consistent with the eq 11. The optimum values of the cross parameters are listed in Table 9.

The ERAS results are compared with experimental V^E_m data along with physical and chemical contributions in Table 10 and Figures 1 and 3. The standard deviations are in the range 0.058 to 0.101 × 10^6 m$^3\cdot$mol^{-1} for DIPE−aniline and 0.124 to 0.266 × 10^6 m$^3\cdot$mol^{-1} for oxolane−aniline. It is important to note that in oxolane + aniline physical contribution is positive and chemical contribution negative while in case of DIPE + aniline both the physical and chemical contributions are large negative with almost of equal importance.

Table 10. Chemical and Physical Contributions to Total ERAS V^E_m and Difference between Experiment and Model Results for DIPE + Aniline and Oxolane + Aniline

x_1	$10^6 V^E_{chem}$ / m$^3\cdot$mol^{-1}	$10^6 V^E_{phy}$ / m$^3\cdot$mol^{-1}	$10^6 V^E_{ERAS}$ / m$^3\cdot$mol^{-1}	$10^6 \delta V^E_{Expt-ERAS}$ / m$^3\cdot$mol^{-1}
		DIPE + Aniline at 303.15 K		
0.0707	−0.302	−0.390	−0.691	−0.048
0.1488	−0.580	−0.756	−1.336	−0.064
0.2307	−0.808	−1.073	−1.881	−0.062
0.3178	−0.980	−1.322	−2.302	−0.097
0.4169	−1.089	−1.497	−2.586	−0.102
0.5201	−1.109	−1.554	−2.663	−0.072
0.6208	−1.040	−1.483	−2.522	0.025
0.7396	−0.848	−1.230	−2.078	0.216
		DIPE + Aniline at 313.15 K		
0.0707	−0.383	−0.453	−0.836	−0.038
0.1488	−0.748	−0.882	−1.630	−0.041
0.2307	−1.059	−1.256	−2.315	−0.033
0.3178	−1.307	−1.553	−2.860	−0.042
0.4169	−1.482	−1.767	−3.249	−0.050
0.5201	−1.541	−1.842	−3.383	−0.045
0.6208	−1.472	−1.771	−3.243	−0.007
0.7396	−1.227	−1.478	−2.705	0.061
0.8673	−0.752	−0.899	−1.651	0.139
		DIPE + Aniline at 323.15 K		
0.0707	−0.477	−0.520	−0.997	−0.009
0.1488	−0.943	−1.019	−1.962	−0.007
0.2307	−1.352	−1.449	−2.801	0.022
0.3178	−1.691	−1.798	−3.489	0.026
0.4169	−1.945	−2.054	−3.999	0.046
0.5201	−2.048	−2.158	−4.205	0.046
0.6208	−1.978	−2.079	−4.057	−0.005
0.7396	−1.664	−1.746	−3.410	−0.083
0.8673	−1.025	−1.074	−2.099	−0.131
		Oxolane + Aniline at 303.15 K		
0.0870	−0.355	0.045	−0.311	0.105
0.1803	−0.642	0.084	−0.558	0.170
0.2735	−0.835	0.113	−0.722	0.164
0.3573	−0.938	0.135	−0.803	0.118
0.4556	−0.981	0.147	−0.834	−0.013
0.5638	−0.943	0.147	−0.796	−0.140
0.6708	−0.828	0.133	−0.695	−0.187
0.8169	−0.556	0.091	−0.464	−0.058
0.8812	−0.392	0.061	−0.331	−0.012
		Oxolane + Aniline at 313.15 K		
0.0870	−0.446	0.045	−0.401	0.083
0.1803	−0.820	0.085	−0.735	0.183
0.2735	−1.086	0.115	−0.970	0.199
0.3573	−1.235	0.138	−1.097	0.146
0.4556	−1.311	0.151	−1.160	0.054
0.5638	−1.279	0.151	−1.128	−0.067
0.6708	−1.137	0.137	−1.000	−0.185
0.8169	−0.774	0.094	−0.679	−0.189
0.8812	−0.548	0.063	−0.484	−0.176
		Oxolane + Aniline at 323.15 K		
0.0870	−0.527	0.044	−0.483	0.073
0.1803	−0.980	0.082	−0.898	0.268
0.2735	−1.312	0.112	−1.201	0.325
0.3573	−1.508	0.134	−1.374	0.305
0.4556	−1.618	0.147	−1.471	0.142
0.5638	−1.594	0.147	−1.447	−0.043
0.6708	−1.429	0.134	−1.295	−0.222
0.8169	−0.980	0.093	−0.887	−0.426
0.8812	−0.694	0.062	−0.632	−0.330

The ERAS model describes the composition dependence of V^E_m very well for DIPE−aniline (Figure 1) while fails when representing V^E_m of oxolane + aniline mixture (Figure 3). This failure may be ascribed to the fact that model does not take into account dipole−dipole interactions between unlike molecules. Similar discrepancy between experiment and model results were observed in case of aniline + methanol + ethanol.[6]

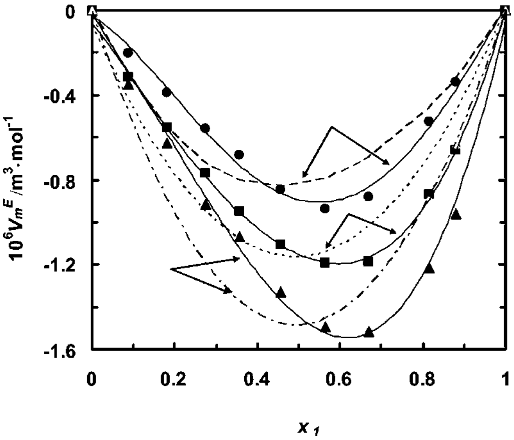

Figure 3. Excess molar volumes of oxolane + aniline, Solid line experimental points at T = ●, 303.15 K; ■, 313.15 K; ▲, 323.15 K from ref 17. Dashed lines represent ERAS results.

Conclusions

The values of V_m^E and κ_S^E are large and negative for binary mixtures of DIPE 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 components. The estimation ability of speed of sound in presently investigated mixtures follows the sequence CFT >PFPOT > FLT. The ERAS model describes the composition dependence of V_m^E very well for DIPE-aniline, while fails when representing V_m^E of oxolane + aniline mixture.

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