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Thermoacoustic Properties of Binary Liquid Mixtures of Sulfolane with Aniline, *N*,*N*-Dimethylaniline and *N*,*N*-Diethylaniline at Different Temperatures and Atmospheric Pressure

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Densities and sound velocities of the binary liquid mixtures of sulfolane + aniline, sulfolane + *N*,*N*-dimethylaniline, sulfolane + *N*,*N*-diethylaniline over the whole range of composition and their pure component were measured at temperatures (T = 303.15, 308.15, 313.15 K) and atmospheric pressure. A high precision vibrating-tube densitometer was used for the measurements. From the measured values, excess adiabatic compressibility (β_s^E), excess sound velocity (u^E), excess internal pressure (P_i^E) and deviation of surface tension ($\Delta\gamma$) were calculated for each of the systems. The excess properties and surface tension deviation were fitted to the Redlich-Kister equation. All these properties have been discussed in terms of molecular interactions.

Keywords: Sulfolane, Aniline, *N*,*N*-Dimethylaniline, *N*,*N*-Diethylaniline, Binary mixture.

INTRODUCTION

The studies of thermodynamic and acoustic properties of binary liquid mixtures have been extensively proved to be a useful tool in elucidating the nature and strength of intermolecular interactions and geometrical effects that are operating between component molecules [1-4]. These mentioned properties are widely used in many known fields of scientific research including physics, chemistry, biology, medicines and some industrial processes such as separation of chemicals, fluid flow, heat flow or chemical reactions, and extremely useful in controlling the process parameters and manufacturing equipment with the accurate design. These properties can also be used for the development of molecular models for describing the actual behaviour of the solution [5-7].

The liquids were selected for the present investigation based on their industrial importance. Sulfolane is an important industrial solvent that has several advantageous physico-chemical properties and the ability to extract monocyclic aromatic hydrocarbons from petroleum products. Mixtures of sulfolane with other solvents are also of particular interest. Aromatic amines may be sulfonated with sulphuric acid in the presence of sulfolane. Sulphanilic acid and aromatic sulphonic acids can be made by the sulphonation of aniline and other aromatic compounds. An understanding of the mixing behaviour of sulfolane with aniline and substituted aniline is therefore immensely important and has applications in many engineering areas as well as synthetic chemistry.

To the best of our knowledge, no extensive studies have been made on the mixtures of sulfolane with aniline and substituted aniline. Thus keeping both industrial and scientific interests in mind, the densities (ρ) and sound velocities (u) of binary liquid mixtures of sulfolane with aniline, *N*,*N*-dimethylaniline and *N*,*N*-diethylaniline were measured over the entire composition range at T = (303.15, 308.15 and 313.15) K under atmospheric pressure. With this data, volumetric and transport properties were calculated and reported [8]. From the measured data, excess adiabatic compressibility (β_s^E), excess sound velocity (u^E), excess internal pressure (P_i^E) and deviation of surface tension ($\Delta\gamma$) were computed. These results were used to gain a better understanding of the intermolecular interactions between the component molecules of the liquid mixtures.

EXPERIMENTAL

The chemicals sulfolane (Sigma-Aldrich, GC grade, purity ≥ 0.99), aniline (Thomas Baker, GLC grade, purity ≥ 0.99), *N,N*-dimethylaniline (BDH, GC grade, purity ≥ 0.99) and *N,N*-diethylaniline (Merck, GC grade, purity ≥ 0.99) were used without further purification.

Procedures: Binary liquid mixtures were prepared by weighting mass using a balance (Mettler Toledo, B204-S, Switzerland) with a stated precision of ±0.0001 g and the masses of the components were converted to their corresponding mole fractions. From the uncertainties of masses of components derived from the accuracy of balance and purities of samples, the standard uncertainty in mole fractions was estimated to be 1×10^{-4}. Mixtures were allowed to stand for some time before every measurement to avoid air bubbles.

The densities and sound velocities of the pure liquid and binary liquid mixtures were measured using a high precision vibrating tube digital density meter and sound velocity analyzer (model DSA 5000, Anton-Paar, Austria). The density meter cell was calibrated with deionized double-distilled water and dry air at atmospheric pressure. This instrument kept the samples at working temperature with a resolution of 0.001 K. By measuring the damping of the oscillation of U-tube caused by the viscosity of the filled sample, the DSA 5000 automatically corrects viscosity related errors on density. The standard uncertainty of density and sound velocity measurement of the density meter was 1×10^{-3} kg m^{-3} and 0.1 m s^{-1}. Considering the contribution of sample impurity to the uncertainty [9] the standard uncertainties for measurements were estimated to be 0.01 K for temperature, 0.1 kg m^{-3} for density and 0.2 m s^{-1} for sound velocity. The comparison of experimental densities and sound velocities of pure liquids were made with literature values in Table-1. It is found that the agreement between experimental and literature values are excellent.

Theory and calculations

From the measured values of density (ρ) and sound velocity (u), adiabatic compressibility (β_s) of the pure liquids and their mixtures were calculated by using the Newton-Laplace relation:

$$\beta_s = -\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial P}\right) = \frac{1}{\rho u^2} \tag{1}$$

The excess adiabatic compressibility was calculated by using the relation:

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

where β_s^{id} is adiabatic compressibility of the ideal mixture, which is calculated by using the relations:

$$\beta_s^{id} = \sum_{i=1}^{2} \phi_i \beta_i \tag{3}$$

and

$$\phi_i = x_i V_{m,i} \Big/ \sum_{i=1}^{2} x_i V_{m,i} = x_i \left(\frac{M_i}{\rho_i}\right) \Big/ \sum_{i=1}^{2} x_i \left(\frac{M_i}{\rho_i}\right) \tag{4}$$

where ϕ_i, x_i, Vm, i, M_i and ρ_i are the volume fraction, mole fraction, molar volume, molar mass and density of the individual pure components respectively.

The excess sound velocity of binary liquid mixtures was calculated by the relations:

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

where,

$$u^{id} = \left(\rho^{id} \beta_s^{id}\right)^{-1/2} \tag{6}$$

and

$$\rho^{id} = \sum_{i=1}^{2} \phi_i \rho_i \tag{7}$$

Assuming the thermodynamic equation of state internal pressure (P_i) can be defined as;

$$P_i = \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V = P \tag{8}$$

where U is the internal energy, V is volume, P is the external pressure and T is temperature. Considering the isobaric coeffi-

TABLE-1
COMPARISON OF EXPERIMENTAL DENSITIES, SOUND VELOCITIES (u) OF PURE LIQUIDS WITH LITERATURE VALUES AT DIFFERENT TEMPERATURES AND ATMOSPHERIC PRESSURE (P = 101 kPa)[a]

Compounds	Temp. (K)	ρ (kg m^{-3})		u (m s^{-1})	
		Exp.	Lit.	Exp.	Lit.
Sulfolane	303.15	1260.132	1261.8 [10], 1262.9 [11]	1582.6	1588.00 [12]
	308.15	1255.726	1257.0 [10]	1566.7	
	313.15	1251.325	1251.6 [10], 1254.1 [11]	1550.9	1558.00 [12]
Aniline	303.15	1013.042	1012.9 [13]	1618.2	1619.20 [14], 1617.00 [15]
	308.15	1008.899	1008.6 [13]	1598.9	1611.00 [16]
	313.15	1004.355	1004.2 [13]	1579.7	1582.00 [17], 1602.00 [16]
N,N-Dimethylaniline	303.15	947.766	948.0 [18], 947.67 [19]	1466.44	1479.00 [20]
	308.15	943.547	943.55 [19]	1446.69	
	313.15	939.427	938.50 [18]	1427.06	
N,N-Diethylaniline	303.15	925.914	926.0 [18], 925.29 [21]	1433.39	1434.00 [22]
	308.15	921.887	921.26 [21]	1413.56	
	313.15	917.852	917.7 [18]	1393.92	

[a]Standard combined uncertainties u_c are $u_c(u) = 0.2$ m s^{-1}, $u_c(x_2) = 1.10^{-4}$, $u_c(T) = 0.01$ K and $u_c(P) = 2$ kPa
All density values and comparison of densities were represented as in previous article [8].

cient of thermal expansion (α_p) and isothermal compressibility coefficient (β_T), Renuncio *et al.* [23] proposed the following equation for the internal pressure of liquid and liquid mixture:

$$P_i = T\left(\frac{\alpha_p}{\beta_T}\right) - P \qquad (9)$$

$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha_p}{\beta_T}$ term is frequently called the isochoric thermal pressure coefficient.

Pandey and Sanguri [24] used the empirical formula for α_p and β_T in terms of ultrasonic velocity (u), density (ρ) and temperature (T) as follows:

$$\alpha_p(K^{-1}) = 75.6\times10^{-3}T^{-1/9}u^{-1/2}\rho^{-1/3} \qquad (10)$$

$$\beta_T(Pa^{-1}) = 1.71\times10^{-3}T^{-4/9}\rho^{-4/3}u^{-2} \qquad (11)$$

The excess internal pressure (P_i^E), of the liquid mixture is calculated by the equation [25,26]:

$$P_i^E = T\left(\frac{\alpha_p}{\beta_T}\right) - T\left(\sum_{i=1}^{2}\phi_i\alpha_{pi}\Big/\sum_{i=1}^{2}\phi_i\beta_{Ti}\right) \qquad (12)$$

The surface tension (γ) and deviation of surface tension ($\Delta\gamma$), can be obtained from the following equation [27,28]:

$$\gamma = 6.3\times10^{-4}\rho u^{3/2}T^{1/3} \qquad (13)$$

$$\Delta\gamma = \gamma - \sum_{i=1}^{2}x_i\gamma_i \qquad (14)$$

RESULTS AND DISCUSSION

The values of density (ρ), sound velocity (u), excess adiabatic compressibility (β_s^E), excess sound velocity (u^E), excess internal pressure (P_i^E) and deviation of surface tension ($\Delta\gamma$), are listed in Table-2 as a function of composition and temperature.

The values of β_s^E, u^E, P_i^E and $\Delta\gamma$ are fitted to Redlich-Kister [29] type polynomial equation:

$$Y = x_2(1-x_2)\sum_{i=0}^{3}A_i(1-2x_2)^i \qquad (15)$$

where Y = β_s^E, u^E, P_i^E and $\Delta\gamma$ are the adjustable parameters of the function and determined using the least-squares method. The corresponding standard deviations of fit, σ(Y) are computed using the relation:

$$\sigma(Y) = \left(\frac{(Y_{exp}-Y_{cal})^2}{(n-m)}\right)^{1/2} \qquad (16)$$

where, n is the total number of experimental points and m is the number of coefficients in eqn. 15. The coefficients (A_i) in eqn. 15 and the standard deviations of all the binary mixtures are presented in Table-3.

Table-2 reveals that the values of β_s^E are negative for all the studied systems over the entire composition range and these values increase with increasing the temperature. Negative

TABLE-2
DENSITY (ρ), SOUND VELOCITY (u), EXCESS ADIABATIC COMPRESSIBILITY (β_s^E), EXCESS INTERNAL PRESSURE (P_i^E) AND DEVIATION OF SURFACE TENSION ($\Delta\gamma$) OF (x_1) SULFOLANE + (x_2) ANILINE, (x_1) SULFOLANE + (x_2) *N,N*-DIMETHYLANILINE AND (x_1) SULFOLANE + (x_2) *N,N*-DIETHYLANILINE AT DIFFERENT TEMPERATURES, T = (303.15, 308.15 AND 313.15) K AND ATMOSPHERIC PRESSURE (P = 101 kPa[a])

x_1	ρ (kg m^{-3})	u (m s^{-1})	10^{10} β_s^E (m^2 N^{-1})	10^{-2} u^E (m s^{-1})	10^{-11} P_i^E (N m^{-2})	10^{-3} $\Delta\gamma$ (N m^{-1})
(x_1) sulfolane + (x_2) aniline						
Temp. (K) = 303.15						
0.0000	1013.0	1618.2	0.000	0.000	0.000	0.000
0.1005	1040.8	1616.3	-0.030	0.048	0.520	0.217
0.2018	1068.3	1614.1	-0.052	0.086	0.951	0.398
0.2973	1093.4	1611.3	-0.064	0.107	1.219	0.499
0.3997	1119.6	1607.6	-0.068	0.115	1.373	0.546
0.5003	1144.7	1603.7	-0.067	0.115	1.416	0.550
0.6098	1171.4	1599.2	-0.060	0.104	1.337	0.506
0.6993	1192.6	1596.0	-0.053	0.094	1.210	0.459
0.8045	1217.0	1591.6	-0.039	0.070	0.927	0.352
0.9000	1238.3	1587.5	-0.022	0.041	0.542	0.206
1.0000	1260.1	1582.6	0.000	0.000	0.000	0.000
Temp. (K) = 308.15						
0.0000	1008.7	1598.9	0.000	0.000	0.000	0.000
0.1005	1036.5	1597.7	-0.033	0.052	0.528	0.228
0.2018	1064.0	1596.1	-0.057	0.092	0.967	0.414
0.2973	1089.1	1593.7	-0.070	0.114	1.239	0.518
0.3997	1115.3	1590.5	-0.075	0.124	1.396	0.568
0.5003	1140.3	1586.9	-0.073	0.123	1.439	0.567
0.6098	1167.0	1582.7	-0.065	0.111	1.359	0.522
0.6993	1188.3	1579.6	-0.057	0.099	1.230	0.471
0.8045	1212.6	1575.4	-0.042	0.074	0.943	0.356
0.9000	1233.9	1571.4	-0.024	0.043	0.551	0.207
1.0000	1255.7	1566.7	0.000	0.000	0.000	0.000
Temp. (K) = 313.15						
0.0000	1004.4	1579.7	0.000	0.000	0.000	0.000
0.1005	1032.2	1579.3	-0.036	0.056	0.537	0.240
0.2018	1059.7	1578.2	-0.063	0.098	0.982	0.429
0.2973	1084.8	1576.2	-0.076	0.122	1.259	0.536
0.3997	1111.0	1573.4	-0.081	0.132	1.418	0.588
0.5003	1136.0	1570.1	-0.079	0.131	1.463	0.586
0.6098	1162.7	1566.2	-0.071	0.118	1.381	0.538
0.6993	1183.9	1563.1	-0.061	0.104	1.250	0.479
0.8045	1208.2	1559.2	-0.045	0.077	0.958	0.363
0.9000	1229.5	1555.4	-0.025	0.045	0.560	0.209
1.0000	1251.3	1550.9	0.000	0.000	0.000	0.000
(x_1) sulfolane + (x_2) *N,N*-dimethylaniline						
Temp. (K) = 303.15						
0.0000	947.7	1466.4	0.000	0.000	0.000	0.000
0.0869	970.8	1475.9	-0.063	0.079	0.706	-0.278
0.2020	1001.6	1488.5	-0.125	0.170	1.527	-0.613
0.3035	1029.6	1499.2	-0.159	0.231	2.128	-0.869
0.3913	1054.8	1508.8	-0.179	0.273	2.579	-1.020
0.4999	1087.4	1520.9	-0.189	0.305	2.994	-1.121
0.5945	1117.3	1531.7	-0.184	0.313	3.195	-1.114
0.7011	1152.7	1544.1	-0.162	0.292	3.139	-1.003
0.7827	1181.0	1553.7	-0.132	0.248	2.808	-0.844
0.8944	1221.1	1567.7	-0.074	0.148	1.808	-0.493
1.0000	1260.1	1582.6	0.000	0.000	0.000	0.000

Temp. (K) = 308.15						
0.0000	943.5	1446.7	0.000	0.000	0.000	0.000
0.0869	967.0	1456.0	-0.065	0.075	0.717	-0.284
0.2020	997.9	1468.7	-0.130	0.165	1.553	-0.625
0.3035	1026.2	1479.9	-0.169	0.229	2.163	-0.864
0.3913	1051.5	1489.8	-0.190	0.272	2.622	-1.014
0.4999	1084.3	1502.2	-0.201	0.304	3.043	-1.109
0.5945	1114.2	1513.3	-0.195	0.312	3.247	-1.104
0.7011	1149.5	1526.1	-0.171	0.290	3.191	-0.998
0.7827	1177.7	1536.1	-0.140	0.247	2.855	-0.839
0.8944	1217.4	1550.7	-0.077	0.145	1.838	-0.497
1.0000	1255.7	1566.7	0.000	0.000	0.000	0.000
Temp. (K) = 313.15						
0.0000	939.4	1427.1	0.000	0.000	0.000	0.000
0.0869	963.2	1436.2	-0.068	0.072	0.729	-0.289
0.2020	994.4	1448.9	-0.135	0.160	1.578	-0.635
0.3035	1022.8	1460.9	-0.179	0.228	2.198	-0.858
0.3913	1048.4	1470.9	-0.202	0.270	2.664	-1.004
0.4999	1081.2	1483.7	-0.213	0.304	3.093	-1.098
0.5945	1111.1	1495.1	-0.207	0.310	3.300	-1.098
0.7011	1146.4	1508.2	-0.181	0.288	3.242	-0.990
0.7827	1174.4	1518.6	-0.147	0.245	2.901	-0.835
0.8944	1213.9	1534.0	-0.082	0.144	1.868	-0.486
1.0000	1251.3	1550.9	0.000	0.000	0.000	0.000
(x_1) sulfolane + (x_2) *N,N*-diethylaniline						
Temp. (K) = 303.15						
0.0000	925.9	1433.4	0.000	0.000	0.000	0.000
0.1009	947.7	1442.7	-0.058	0.073	0.582	-0.769
0.2001	970.8	1451.8	-0.099	0.133	1.178	-1.502
0.2977	995.4	1461.3	-0.131	0.185	1.724	-2.108
0.3973	1022.7	1471.6	-0.151	0.226	2.244	-2.614
0.4999	1053.7	1484.5	-0.173	0.266	2.653	-2.853
0.5999	1086.9	1499.0	-0.174	0.293	3.134	-2.961
0.7007	1124.0	1515.8	-0.168	0.299	3.294	-2.736
0.7992	1164.1	1534.3	-0.140	0.266	3.076	-2.238
0.9001	1209.5	1557.4	-0.092	0.186	2.159	-1.301
1.0000	1260.1	1582.6	0.000	0.000	0.000	0.000
Temp. (K) = 308.15						
0.0000	921.9	1413.6	0.000	0.000	0.000	0.000
0.1009	943.7	1423.3	-0.063	0.075	0.591	-0.761
0.2001	966.8	1432.7	-0.107	0.137	1.197	-1.491
0.2977	991.4	1442.5	-0.141	0.190	1.752	-2.093
0.3973	1018.8	1453.1	-0.162	0.232	2.281	-2.593
0.4999	1049.7	1466.2	-0.185	0.272	2.697	-2.838
0.5999	1082.9	1481.2	-0.187	0.301	3.185	-2.942
0.7007	1120.0	1498.4	-0.179	0.306	3.348	-2.720
0.7992	1160.0	1517.3	-0.149	0.272	3.127	-2.229
0.9001	1205.2	1540.8	-0.098	0.190	2.194	-1.302
1.0000	1255.7	1566.7	0.000	0.000	0.000	0.000
Temp. (K) = 313.15						
0.0000	917.9	1393.9	0.000	0.000	0.000	0.000
0.1009	939.7	1403.9	-0.067	0.077	0.601	-0.757
0.2001	962.8	1413.6	-0.114	0.140	1.217	-1.481
0.2977	987.4	1423.8	-0.151	0.194	1.780	-2.079
0.3973	1014.8	1434.7	-0.174	0.237	2.318	-2.577
0.4999	1045.7	1448.2	-0.199	0.279	2.741	-2.817
0.5999	1078.8	1463.5	-0.199	0.308	3.237	-2.925
0.7007	1116.2	1481.0	-0.192	0.313	3.402	-2.697
0.7992	1155.8	1500.0	-0.157	0.275	3.177	-2.234
0.9001	1200.9	1523.9	-0.101	0.190	2.230	-1.321
1.0000	1251.3	1550.9	0.000	0.000	0.000	0.000

[a] Standard combined uncertainties u_c are $u_c(\rho) = 0.1$ kg m^{-2}, $u_c(u) = 0.2$ m s^{-1}, $\underline{u}_c(x_2) = 1 \times 10^{-4}$, $u_c(T) = 0.01$ K and $u_c(P) = 2$ kPa

All density values were obtained from the previous article [8].

values of β_s^E specify that these mixtures are less compressible than the corresponding ideal mixtures due to the association of unlike molecules in these solutions. The negative values of β_s^E are the indication of strong interaction and the values of β_s^E tend to become increasingly negative when the strength of the interaction between the components increases whereas positive values of β_s^E reflect the weak interaction between unlike molecules [2,30].

The negative values of β_s^E may be due to chemical or specific interactions including hydrogen bonding, dipole-dipole interactions among the unlike components, attractive London dispersion forces [31] and favorable geometrical fitting *i.e.* interstitial accommodation of one component into another due to the differences in the molar volume and free volume between components, whereas physical or non-specific interaction involves the disruption of native molecular packing of pure liquids may contribute to positive β_s^E values [32,33].

Fig. 1 represents the comparison of β_s^E values for all binary mixture at 303 K. The values of β_s^E for sulfolane + aniline system are less negative and more negative for sulfolane + *N,N*-dimethylaniline whereas, the values of β_s^E for sulfolane + *N,N*-diethylaniline are almost comparable with sulfolane + *N,N*-dimethylaniline at their corresponding minima. In our present study, all the liquids used are polar and the dipole moments of sulfolane [15], aniline [16], *N,N*-dimethylaniline [16] and *N,N*-diethylaniline [16] are 4.7 D, 1.79 D, 1.84 D and 1.64 D, respectively. Aniline and substituted aniline possess π-electron clouds on the aromatic ring and electron density would increase with increasing the electron donating ability of substituent attached to the nitrogen atom. Aniline is susceptible to form a hydrogen bond with sulfolane, but *N,N*-dimethylaniline and *N,N*-diethylaniline are unable to form a hydrogen bond with sulfolane due to the replacement of hydrogen attached to nitrogen by alkyl groups. Further, the molar volumes of sulfolane (95.3654 cm^3 mol^{-1}) and aniline (91.9274 cm^3 mol^{-1}) at $T = 303.15$ K are almost comparable, while there is a remarkable difference

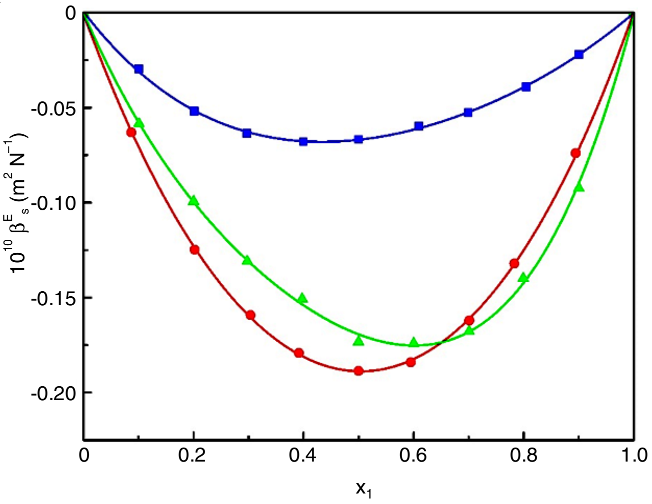

Fig. 1. Excess adiabatic compressibility (β_s^E) as a function of mole fraction of sulfolane (x_1) at temperature of 303.15 K for the binary mixtures of sulfolane + aniline (■), sulfolane + *N,N*-dimethylaniline (●) and sulfolane + *N,N*-diethylaniline (▲). The solid lines represent the fitting values according to eqn. 15

TABLE-3
COEFFICIENTS (A_i) AND STANDARD DEVIATION OF FIT (σ) OF REDLICH-KISTER EQUATION (eqn. 15) AT DIFFERENT TEMPERATURES, T = (303.15, 308.15 AND 313.15) K AND ATMOSPHERIC PRESSURE (P = 101 kPa)

Property	T (K)	A_0	A_1	A_2	A_3	σ
(x_1) sulfolane + (x_2) aniline						
$10^{10}\ \beta_s^E$ ($m^2\ N^{-1}$)	303.15	-0.2677 ± 0.0014	0.0749 ± 0.0052	-0.0416 ± 0.0062	-0.037 ± 0.0137	0.0000024
	308.15	-0.2926 ± 0.0013	0.0852 ± 0.0050	-0.0427 ± 0.0059	-0.034 ± 0.0130	0.0000022
	313.15	-0.3189 ± 0.0010	0.0971 ± 0.0040	-0.0453 ± 0.0047	-0.032 ± 0.0103	0.0000014
$10^{-2}\ u^E$ ($m\ s^{-1}$)	303.15	0.4602 ± 0.0025	-0.1021 ± 0.0097	0.0759 ± 0.0115	0.0853 ± 0.0252	0.0000082
	308.15	0.4929 ± 0.0022	-0.1155 ± 0.0086	0.0684 ± 0.0102	0.0841 ± 0.0224	0.0000064
	313.15	0.5241 ± 0.0015	-0.1290 ± 0.0056	0.0678 ± 0.0067	0.0814 ± 0.0147	0.0000028
$10^{-11}\ P_i^E$ ($N\ m^{-2}$)	303.15	5.6755 ± 0.0200	-0.2339 ± 0.0774	0.5013 ± 0.0917	0.6316 ± 0.2020	0.0005200
	308.15	5.7691 ± 0.0204	-0.2377 ± 0.0787	0.5096 ± 0.0932	0.6421 ± 0.2053	0.0005400
	313.15	5.8627 ± 0.0207	-0.2416 ± 0.0800	0.5179 ± 0.0947	0.6525 ± 0.2087	0.0005600
$10^{-3}\ \Delta\gamma$ ($N\ m^{-1}$)	303.15	2.2066 ± 0.0140	-0.3482 ± 0.0542	0.3314 ± 0.0642	0.4399 ± 0.1414	0.0002600
	308.15	2.2832 ± 0.0130	-0.3857 ± 0.0501	0.3088 ± 0.0592	0.3795 ± 0.1306	0.0002200
	313.15	2.3558 ± 0.0102	-0.4332 ± 0.0392	0.2946 ± 0.0464	0.3613 ± 0.1023	0.0001300
(x_1) sulfolane + (x_2) *N,N*-dimethylaniline						
$10^{10}\ \beta_s^E$ ($m^2\ N^{-1}$)	303.15	-0.7552 ± 0.0010	-0.0303 ± 0.0038	-0.0532 ± 0.0047	0.0613 ± 0.0101	0.0000013
	308.15	-0.8026 ± 0.0003	-0.0326 ± 0.0011	-0.0280 ± 0.0013	0.0517 ± 0.0029	0.0000001
	313.15	-0.8518 ± 0.0012	-0.0283 ± 0.0044	-0.0112 ± 0.0055	0.0192 ± 0.0118	0.0000018
$10^{-2}\ u^E$ ($m\ s^{-1}$)	303.15	1.2233 ± 0.0019	0.3772 ± 0.0073	0.1057 ± 0.0090	-0.0473 ± 0.0193	0.0000048
	308.15	1.2207 ± 0.0016	0.3799 ± 0.0062	0.0567 ± 0.0077	-0.0287 ± 0.0166	0.0000035
	313.15	1.2170 ± 0.0021	0.3769 ± 0.0079	0.0207 ± 0.0098	0.0092 ± 0.0212	0.0000057
$10^{-11}\ P_i^E$ ($N\ m^{-2}$)	303.15	11.9788 ± 0.0103	6.0078 ± 0.0394	3.3135 ± 0.0487	0.6345 ± 0.1050	0.0001400
	308.15	12.1764 ± 0.0105	6.1069 ± 0.0400	3.3681 ± 0.0495	0.6449 ± 0.1067	0.0001400
	313.15	12.3740 ± 0.0106	6.2060 ± 0.0407	3.4228 ± 0.0503	0.6554 ± 0.1085	0.0001500
$10^{-3}\ \Delta\gamma$ ($N\ m^{-1}$)	303.15	-4.4739 ± 0.0075	-0.8151 ± 0.0286	0.1777 ± 0.0354	-0.4099 ± 0.0763	0.0000740
	308.15	-4.4283 ± 0.0037	-0.7794 ± 0.0142	-0.0047 ± 0.0176	-0.4036 ± 0.0380	0.0000180
	313.15	-4.3895 ± 0.0071	-0.8073 ± 0.0273	-0.0757 ± 0.0338	-0.1560 ± 0.0728	0.0000670
(x_1) sulfolane + (x_2) *N,N*-diethylaniline						
$10^{10}\ \beta_s^E$ ($m^2\ N^{-1}$)	303.15	-0.6772 ± 0.0056	-0.2140 ± 0.0220	-0.2190 ± 0.0258	-0.0219 ± 0.0574	0.000042
	308.15	-0.7265 ± 0.0054	-0.2258 ± 0.0210	-0.2274 ± 0.0247	-0.0120 ± 0.0548	0.000038
	313.15	-0.7793 ± 0.0058	-0.2440 ± 0.0228	-0.2151 ± 0.0268	0.0242 ± 0.0595	0.000045
$10^{-2}\ u^E$ ($m\ s^{-1}$)	303.15	1.0618 ± 0.0057	0.6386 ± 0.0221	0.5575 ± 0.0260	0.2046 ± 0.0577	0.000042
	308.15	1.0882 ± 0.0058	0.6543 ± 0.0226	0.5681 ± 0.0266	0.1967 ± 0.0591	0.000044
	313.15	1.1168 ± 0.0057	0.6759 ± 0.0223	0.5378 ± 0.0262	0.1417 ± 0.0582	0.000043
$10^{-11}\ P_i^E$ ($N\ m^{-2}$)	303.15	10.8406 ± 0.0644	8.7604 ± 0.2516	6.8706 ± 0.2955	3.3397 ± 0.6571	0.005400
	308.15	11.0194 ± 0.0654	8.9049 ± 0.2557	6.9839 ± 0.3004	3.3947 ± 0.6680	0.005600
	313.15	11.1982 ± 0.0665	9.0494 ± 0.2599	7.0972 ± 0.3053	3.4498 ± 0.6788	0.005800
$10^{-3}\ \Delta\gamma$ ($N\ m^{-1}$)	303.15	-11.5613 ± 0.0467	-3.6245 ± 0.1825	-0.0955 ± 0.2143	-0.3042 ± 0.4766	0.002900
	308.15	-11.4826 ± 0.0421	-3.6076 ± 0.1644	-0.1444 ± 0.1931	-0.4084 ± 0.4294	0.002300
	313.15	-11.3908 ± 0.0429	-3.5325 ± 0.1678	-0.3560 ± 0.1971	-0.7796 ± 0.4382	0.002400

in molar volume of *N,N*-dimethylaniline (127.8722 $cm^3\ mol^{-1}$) and *N,N*-diethylaniline (161.1737 $cm^3\ mol^{-1}$) from sulfolane [8]. Thus, the absence of the structural effect in the sulfolane + aniline system and small dipole moment of *N,N*-diethylaniline give rise their β_s^E values less negative, whereas the result of structural effect and large dipole moment of N,N-dimethylaniline makes its β_s^E values more negative.

Table-2 indicates that u^E values are positive over the entire composition range for all the binary mixtures at all experimental temperatures and these values increase with increasing temperature. Positive values of u^E indicate the strong interaction of component molecules of the binary liquid mixture [34]. If strong interactions arise among the components of a mixture leading to the formation of molecular aggregates and making more compact structures, then the sound will travel faster through the mixture by means of longitudinal waves and hence the speed of sound deviations with respect to a linear behaviour will be positive. While, if structure-breaking factors in the mixture predominate, resulting in the expansion, then the sound velocity through the mixture will be slow, resulting negative deviation in the sound velocity. Fig. 2 reveals that the values of u^E for sulfolane + aniline system are less positive compared to sulfolane + *N,N*-dimethylaniline and sulfolane + *N,N*-diethylaniline at their corresponding maxima at 303 K. Although, due to H-bonding in sulfolane + aniline, sound should travels faster compared to others two binary mixtures but due to the structural effect opposite trend is observed, which is consistence with β_s^E values.

Positive deviation of P_i^E values are observed over the whole range of composition for all the binary mixtures at all investigated temperatures (Table-2). In addition, positive deviation of P_i^E values increase with increasing temperature similar to u^E values. The positive deviation in excess internal pressure suggests that there exist strong interactions between the compo-

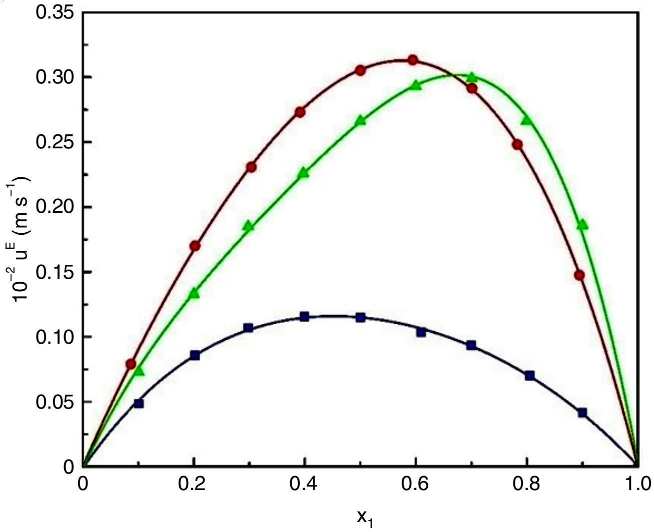

Fig. 2. Excess sound velocity (u^E) as a function of mole fraction of sulfolane (x_1) at temperature of 303.15 K for the binary mixtures of sulfolane + aniline (■), sulfolane + *N,N*-dimethylaniline (●) and sulfolane + *N,N*-diethylaniline (▲). The solid lines represent the fitting values according to eqn. 15

nents of the liquid mixture [10]. The cohesive forces, which are the result of forces of attraction and forces of repulsion between liquid molecules, holding a liquid together create a pressure within the liquid, which has been termed as the internal pressure. Dissolved solutes exist under the internal pressure of the medium and their interactions with the solvent arise through hydrogen bonding, charge transfer, Columbic (or) van der Waal's interaction. Thus a solute in the solution is subject to a 'structural pressure' from the solvent and a 'chemical pressure' from interactions with the solvent [3]. To understand the physical significance of internal pressure, one must consider a liquid undergoing a small isothermal volume expansion. Total disruption of all the interactions associated with one mole of liquid will not occur. We might intuitively expect those interactions varying most rapidly near the equilibrium separation in the liquid to make the most significant contribution to internal pressure (P_i) [3]. Although hydrogen bonding varies rapidly with intermolecular separation, a localized and 'chemical' nature prevents its detection by a minute volume expansion. Thus, it may be concluded that internal pressure (P_i) measures the polar and non-polar (non-chemical) interactions within a liquid [3].

Fig. 3 shows that the positive values of P_i^E for sulfolane + *N,N*-dimethylaniline and *N,N*-diethylaniline at 303 K are almost comparable, however, sulfolane + *N,N*-diethylaniline shows highest maxima in comparison with other two binary mixtures. Large positive value for sulfolane + *N,N*-diethylaniline mixture indicates that non-polar (non-chemical) interactions are predominate in this mixture which varies most rapidly near the equilibrium separation, whereas the presence of H-bonding in sulfolane + aniline system and high dipole-dipole interaction in sulfolane + *N,N*-dimethylaniline make their P_i^E less positive.

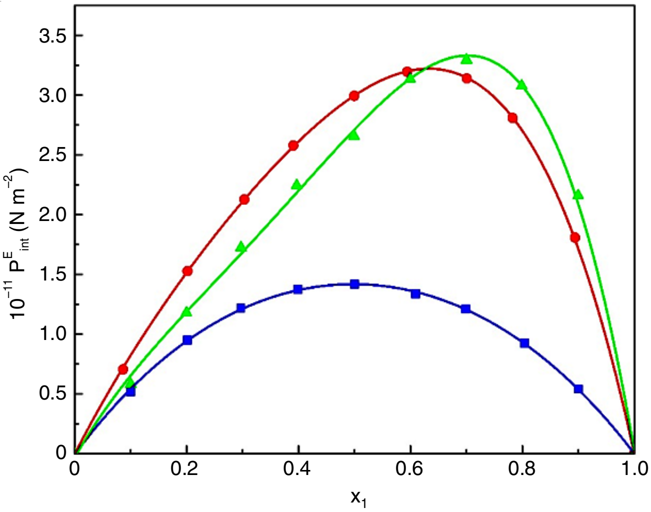

Fig. 3. Excess internal pressure (P^E_{int}) as a function of mole fraction of sulfolane (x_1) at temperature of 303.15 K for the binary mixtures of sulfolane + aniline (■), sulfolane + *N,N*-dimethylaniline (●) and sulfolane + *N,N*-diethylaniline (▲). The solid lines represent the fitting values according to eqn. 15

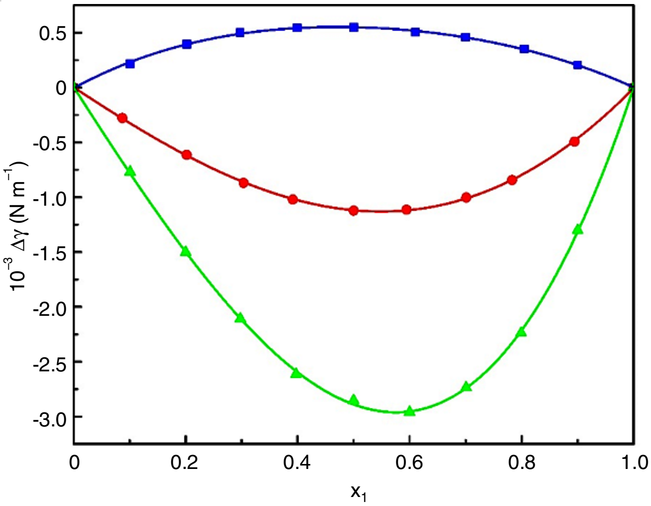

Fig. 4. Deviation of surface tension ($\Delta\gamma$) as a function of mole fraction of sulfolane (x_1) at temperature of 303.15 K for the binary mixtures of sulfolane + aniline (■), sulfolane + *N,N*-dimethylaniline (●) and sulfolane + *N,N*-diethylaniline (▲). The solid lines represent the fitting values according to eqn. 15

Fig. 4 illustrates that the deviation of surface tensions ($\Delta\gamma$), are positive for sulfolane + aniline and sulfolane + *N,N*-dimethylaniline and more positive for sulfolane + *N,N*-dimethylaniline, whereas $\Delta\gamma$ is negative for sulfolane + *N,N*-diethylaniline at all temperatures and compositions. This deviation values also increase with increasing temperatures as indicated by Table-2. Tsierkezos & Filippous [35] suggest that the deviation of surface tension indicate an uneven distribution of the components between the surface region and the bulk region. The negative value of $\Delta\gamma$ indicates that the smaller surface tension components have a higher concentration at the liquid surface than its bulk concentration. According to this, in the sulfolane + aniline and sulfolane + *N,N*-dimethylaniline binary liquid mixtures sulfolane tend to migrate to the surface while aniline and *N,N*-dimethylaniline have a tendency to stay in the bulk. On the other hand in the mixture of sulfolane + *N,N*-diethylaniline, sulfolane tend to stay in the bulk and *N,N*-diethylaniline tend to migrate to the surface.

Conclusion

Densities and sound velocities of pure sulfolane, aniline, *N,N*-dimethylaniline, *N,N*-diethylaniline and their binary mixtures with sulfolane as common component over the entire composition range were measured at T = (303.15, 308.15 and 313.15) K and atmospheric pressure. The experimental data were used to calculate excess adiabatic compressibility, excess sound velocity, excess internal pressure and surface tension deviation. The β_s^E values of all the binary mixtures are negative, while P_i^E and u^E values of all the binary mixtures are positive over the entire composition range at all specified temperatures. Though, values are positive for sulfolane + aniline and sulfolane + *N,N*-dimethylaniline mixtures but negative for sulfolane + *N,N*-diethylaniline mixture over the entire composition range at all experimental temperatures. The positive values of β_s^E and negative values of u^E are due to hydrogen bonding, dipole-dipole interaction and structural effect between unlike molecules, whereas positive values of P_i^E only quantify polar and non-polar interaction. The negative values of $\Delta\gamma$ indicate that the smaller surface tension components have a higher concentration at the liquid surface than its bulk concentration and positive values of $\Delta\gamma$ signify reverse phenomenon.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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