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Investigation Of Molecular Interactions Of Binary Mixtures Contains Phenetole With Aromatic Amines (1º, 2º&3º) At Various Temperatures By Physicochemical, Thermodynamics And FTIR Spectroscopic Analysis''

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Thermophysical parameters such as density (p) of binary liquid mixtures of phenetole (ethoxy benzene) with aniline, N-methyl aniline and N,N-dimethyl aniline have been calculated at temperatures of 303.15 K, 308.15 K & 313.15 K and speed of sound (u) measured at 303.15 K, 313.15 K. The excess molar volumes (V^E) and excess isentropic compressibilities (κ_s^E) of all the studied temperatures have been determined using the data measured from density and speed of sound. Redlich-Kister polynomial equation was fitted to the calculated V^E and κ_s^E values. Additionally, the estimated speed of sound data were compared with Jacobson's Free Length theory (FLT), Nomoto's relationship and Schaff's Collision factor theory (CFT) to test their predictive capability. The results were analyzed in terms of physicochemical interactions occurred due to the solute- solvent components in the binary liquid mixtures. The existence of hydrogen bonding between phenetole and aromatic amines was experimentally confirmed by using AT FT-IR Spectroscopic studies.

Keywords: Density; Speed of sound; FT-IR Spectra: Excess Properties.

Introduction

1. Rationale

To create a wide variety of manufacturing processes and tools, it is required to analyse the physical properties of liquid mixtures [1]. Mixing solvents with other solvents can improve their thermodynamic properties. Combining more than one solvent can result in undesirable mixtures. The excess qualities of mixtures are what differentiate the real property from the ideal property. Polarity influences physical properties as well as the size and shape of the molecules in the liquid mixture. The experimental measurements of these excess properties reveal important details regarding intermolecular interactions and their strength. Additionally, knowledge on the thermophysical characteristics of binary mixtures is useful in both academic and industrial areas [2-3].

The most significant aromatic ether is phenetole, which is widely utilized as an intermediate in the synthesis of many chemical compounds for a variety of useful uses. The intermediate beginning component used in the creation of several derivatives. Phenetole is used as intermediate compound for preparation of different derivatives like dyes, pigment and perfumery. Phenetole is acts as electron pair donor (μ= 1.45 Debye) [4, 5].According to a review of the literature, there have been relatively few studies of the thermophysical properties of binary mixtures of phenetole with isomeric cresol, aryl alcohols, decanol, propylene carbonate, THF,DMF and NMP etc., [6–11].

Amines are used in pharmaceutical, agricultural, and rubber chemical applications. In the manufacturing of dyes, aniline is the starting material. When mixed with other substances, particularly chlorine or chlorates, it produces aniline colours. Aniline is also used to make chemicals for processing rubber, explosives, plastics, antioxidants, varnishes, and other products. Amines have many industrial applications and participate in more chemical reactions. N-Methyl Aniline is used as coupling solvent, agrochemicals, octane booster and an intermediate for manufacture of organic compounds. When making dyes and other substances, N,N-Dimethylaniline is used as an intermediate. Humans have experienced headache, cyanosis, and dizziness as a result of acute (short-term) inhalation exposure to N,N-dimethylaniline. These effects affected the central nervous system (CNS) and circulatory system.

The current study mainly concentrated on the strength of solute-solvent interactions between binary component liquids of Phenetole with Aniline, N-Methyl Aniline and N,N-dimethyl Aniline, on the sign and size of the excess thermophysical properties. The current study is an extension of our past studies on the thermodynamic properties of binary liquid mixtures [12]. Here, we present measurements of the densities and sound speeds for three binary systems like,phenetole + Aniline, phenetole + N-Methyl Aniline, and phenetole + N,N-dimethyl Aniline at T=(303.15-313.15) K at atmospheric pressure. The experimental speed of sound data were examined in terms of Jacobson's free length theory FLT, Schaff's collision factor theory (CFT), and Nomoto's relationship to assess the viability of these theories. In the present study, FT-IR spectral analysis was described in order to comprehend the frequency of H- bonding interaction between phenetole and Aniline, N-Methyl Aniline and N,N-dimethyl Aniline.

2. Experimental section

2.1. Reagent

S.D. Fine Chem.Ltd, supplied all of the A.R. grade chemicals used in the current study. The water content was determined with the new generation (Ana lab Micro aqua cal 100) Mettle Toledo compact coulometric Karl Fisher Titrate C20, and the purity of these substances is shown in Table 1. The purity of all of the experimental liquids was checked using gas chromatography, which used a capillary column and a flame ionization detector. Table 2 lists pure substance density (p) and sound speed (u) values and compares them to values found in the literature [13-31].

Table 1: Name of the chemical, source, CAS number, purity in mass fraction, purity analysis method and water content in mass fraction of the chemicals used in this work.

Component	Source	CAS number	Purity in mass fraction (as received from supplier	Purity in mass fraction (after purification)	*Analysis method	Water content in mass fraction
Phenetole	S.D.Fine Chemicals.Ltd	103-73-1	>0.99	0.989	GC	0.0003
Aniline	S.D.Fine Chemicals. Ltd	62-53-3	>0.99	0.994	GC	0.0004
N-Methylaniline	S.D.Fine Chemicals. Ltd	100-61-8	>0.98	0.995	GC	0.0006
N,N-dimethylaniline	S.D.Fine Chemicals. Ltd.	121-69-7	>0.99	0.997	GC	0.0005

*GC=Gas Chromatography

2.2. Measurements

2.2.1. Sample preparation

The sample masses were determined using an electronic balance model (ATY224, Shimadzu, India) with a precision or uncertainty of $1x10^{-4}$ g. By syringing known weights of pure liquids into airtight screw-capped glass containers, homogenous binary liquid mixes of phenetole with Aniline, N-Methyl Aniline and N,N-dimethyl Aniline were created over the whole range of

composition. For each system, a set of eleven compositions was created, and it was discovered that the uncertainty in the estimated mole fraction concentrations was less than $1x10^{-4}$.

2.2.2. Density (p), Speed of sound (u) Measurements

The digital densitometer (Rudolph Research Analytical DDM-2911 USA) and ultrasonic interferometer model (Mittal Enterprises, F-05.India) were used to measure the density (p), speed of sound (u), and binary liquid mixtures of phenetole with isomeric cresols at temperatures ranging from 303.15K to 313.15K and 0.1 MPa pressure, respectively. Further information about the experimental equipment and procedure can be found here. The working frequency for the speed of sound (u) measurements range is 2 MHz, and a thermostat with repeatability u(T) = 0.02 K keeps the sample at the desired temperature. Our previous work [12] provided a description of the instrument calibration and measurement specifics. Both the measured density and the speed of sound were found to be within $\pm 5x10^{-5} g.cm^3$ and1 $m.s^{-1}$ of each other's uncertainties. All of the pure component molecules and their binary liquid mixtures were examined, and the results were found to be in good agreement with the values found in the literature (Table 2).

Table 2: Density (ρ) and sound speed (u) values for the pure components along with literature values at temperatures studied and at 0.1 MPa pressure.

T/K	ρ/(g.cm^3)		u/(m.s^{-1})	
	Exp.	Lit.	Exp.	Lit.
Phenetole				
303.15	0.95539	0.95550[a] 0.95660[b] 0.95534[c]	1347.96	1347.82[f] 1347.74[c]
308.15	0.95184	0.95086[d] 0.95220[e] 0.95182[c]		
313.15	0.94682	0.94608[f] 0.94684[c]	1308.68	1308.87[f] 1308.64[c]
Aniline				
303.15	1.01276	1.01278[g] 1.01279[h] 1.01280[i]	1615.60	1615.64[g] 1614.50[m] 1619.00[n]
308.15	1.00862	1.00864[g] 1.00960[j]		

		1.00860[k]		
313.15	1.00448	1.00449[g] 1.00445[i] 1.00446[l]	1580.26	1580.00[g] 1581.40[o] 1579.50[n]
N-Methylaniline				
303.15	0.98174	0.98172[g] 0.98170[l] 0.97820[p]	1549.36	1549.32[g] 1545.50[h] 1548.30[p]
308.15	0.97426	0.97604[g]		
313.15	0.97084	0.97089[g] 0.96980[p] 0.9698[q]	1511.86	1511.84[g] 1512.40[p]
N,N-dimethylaniline				
303.15	0.94818	0.94818[g] 0.94815[r] 0.94840[s] 0.94820[t]	1470.34	1470.24[g] 1468.00[s] 1470.50[t]
308.15	0.94358	0.94355[g] 0.94355[u] 0.94386[v]		
313.15	0.93974	0.93978[g] 0.93970[s] 0.93980[t]	1432.62	1431.00[s] 1435.00[t] 1432.00[g]

Standard uncertainties are u(ρ) $\pm 5 \times 10^{-5}$ g.cm^{-3}, u (u) ± 0.5 m.s^{-1}, u (p) = 1kPa, u (T) ± 0.02 and ±0.05 K for ρ and u measurements respectively.

a-Ref [10];b-Ref [12];c-Ref [13];d-Ref [14];e-Ref [8];f-Ref [15];g-Ref [16];h-Ref [17];i-Ref [18];j-Ref [19];k-Ref [20];l-Ref [21];m-Ref [22];n-Ref [23];o-Ref [24];p-Ref [25];q-Ref [26];r-Ref [27];s-Ref [28];t-Ref [29];u-Ref [30];v-Ref [31];

3. Data, Values and Validation

3.1. Excess volumes (V^E)

The excess volumes (V^E) of binary mixtures of Phenetole with Aniline, N-Methyl Aniline and N,N-dimethyl Aniline were calculated from measured density by using the following formula:

$$V^E / cm^3.mol^{-1} = \frac{x_1M_1 + x_2M_2}{\rho_m} - \left[\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2} \right] \quad (1)$$

Where x_1, x_2, M_1, M_2 and ρ_1, ρ_2 represents the mole fraction, molar mass and density of pure component 1 and 2, respectively and ρ_m is the measured density of the mixture. The excess molar volumes (V^E) values were reported in Table -3 at T= (303.15 to 313.15) K and the V^E data were also graphically presented given in Figure 1 at 303.15K.

Table 3: Molefraction of Phenetole (x_1), densities (ρ), experimental excess volumes (V^E) and predicted excess volumes (Redlich-Kister) at T= 303 K to 313.15 K and 0.1M Pa pressure for the binary mixtures of Phenetole (1) with Aniline, N-methylaniline and N,N-dimethylaniline (2).

x_1	Density(ρ) ($g.cm^{-3}$)	$V^E/cm^3.mol^{-1}$	
		Experimental	Redlich-Kister
Phenetole (1) + Aniline (2)			
T=303.15K			
0.0743	1.00903	-0.190	-0.191
0.1529	1.00475	-0.339	-0.338
0.2363	0.99994	-0.446	-0.444
0.3249	0.99473	-0.518	-0.514
0.4193	0.98912	-0.552	-0.551
0.5199	0.98316	-0.549	-0.555
0.6275	0.97701	-0.522	-0.524
0.7428	0.97048	-0.446	-0.445
0.8666	0.96337	-0.289	-0.288
T=308.15K			
0.0743	1.00512	-0.208	-0.208
0.1529	1.00102	-0.370	-0.370
0.2363	0.99638	-0.489	-0.489
0.3249	0.99129	-0.570	-0.569
0.4193	0.98583	-0.616	-0.614
0.5199	0.97993	-0.615	-0.623
0.6275	0.97388	-0.596	-0.592
0.7428	0.96726	-0.504	-0.504
0.8666	0.96005	-0.328	-0.328
T=313.15K			
0.0743	1.00144	-0.262	-0.260

0.1529	0.99739	-0.442	-0.443
0.2363	0.99256	-0.555	-0.561
0.3249	0.98726	-0.625	-0.627
0.4193	0.98158	-0.660	-0.656
0.5199	0.97557	-0.658	-0.656
0.6275	0.96936	-0.631	-0.628
0.7428	0.96275	-0.552	-0.552
0.8666	0.95547	-0.378	-0.379
Phenetole (1) + N-methylaniline (2)			
T=303.15K			
0.0869	0.97955	-0.051	-0.053
0.1764	0.97734	-0.102	-0.096
0.2686	0.97493	-0.131	-0.129
0.3635	0.97244	-0.150	-0.151
0.4614	0.96984	-0.158	-0.162
0.5624	0.96717	-0.156	-0.160
0.6666	0.96442	-0.144	-0.144
0.7741	0.96156	-0.118	-0.113
0.8852	0.95851	-0.065	-0.066
T=308.15K			
0.0869	0.97263	-0.070	-0.071
0.1764	0.97078	-0.117	-0.116
0.2686	0.96875	-0.144	-0.143
0.3635	0.96662	-0.160	-0.158
0.4614	0.96442	-0.168	-0.165
0.5624	0.96214	-0.167	-0.166
0.6666	0.95980	-0.157	-0.160
0.7741	0.95737	-0.135	-0.141
0.8852	0.95482	-0.097	-0.094
T=313.15K			
0.0869	0.96922	-0.091	-0.089
0.1764	0.96719	-0.136	-0.140
0.2686	0.96496	-0.160	-0.166
0.3635	0.96267	-0.176	-0.176
0.4614	0.96030	-0.183	-0.179
0.5624	0.95786	-0.182	-0.178
0.6666	0.95536	-0.173	-0.172
0.7741	0.95279	-0.153	-0.154
0.8852	0.95001	-0.106	-0.106
Phenetole (1) + N,N-dimethylaniline (2)			
T=303.15K			

0.1002	0.94884	0.009	0.011
0.2004	0.94948	0.019	0.017
0.3005	0.95017	0.025	0.021
0.4006	0.95087	0.027	0.025
0.5006	0.95158	0.028	0.027
0.6006	0.95231	0.028	0.029
0.7005	0.95303	0.026	0.030
0.8004	0.95377	0.024	0.027
0.9002	0.95452	0.020	0.018
T=308.15K			
0.1002	0.94429	0.016	0.017
0.2004	0.94503	0.028	0.028
0.3005	0.94578	0.038	0.036
0.4006	0.94656	0.044	0.041
0.5006	0.94737	0.047	0.045
0.6006	0.9482	0.046	0.047
0.7005	0.94905	0.043	0.046
0.8004	0.94992	0.037	0.040
0.9002	0.95081	0.028	0.026
T=313.15K			
0.1002	0.94031	0.019	0.021
0.2004	0.94090	0.036	0.034
0.3005	0.94154	0.045	0.042
0.4006	0.94222	0.049	0.047
0.5006	0.94291	0.052	0.051
0.6006	0.94362	0.051	0.053
0.7005	0.94434	0.049	0.052
0.8004	0.94509	0.043	0.046
0.9002	0.94588	0.032	0.030

The standard uncertainties are u (x) ± $1x10^{-4}$, u (ρ) ± $5x10^{-5}$ g.cm^{-3}, u (T) = 0.02K and u(p) = 1 kPa, and u (V^E) = ±0.002 cm^3.mol^{-1}.respectively.

Redlich-Kister equation:

$$V^E=x_1x_2[a_0+a_1(x_1-x_2) + a_2(x_1-x_2)^2] \quad (2)$$

Where a_0, a_1, a_2 are adjustable parameters of Redlich-Kister equation and x_i is the mole fraction of component i (i = 1, 2) in the mixture.

The composition, size difference, intermolecular contact strength, and geometry of the constituents all have a significant role in the V^E data of binary liquid mixtures. The sign and magnitude of V^E for the binary liquids had been tormented by the relative energy of several

opposing effects. Those consequences can be categorised especially into three types specifically, chemical, physical and structural effects [1].

An estimation of V^E facts for the mixtures of Phenetole with Aniline and N-methyl Aniline are negative over the whole composition range. But, the mixture of Phenetole with N,N-dimethyl Aniline are positive over the whole composition range. The relative strength of the expansion and contraction caused by the mixing of the two component molecules may have an impact on the sign of excess volume in a binary system. The excess volume (V^E) becomes positive; due to expansion dominate the factors of contraction. On the other hand, V^E becomes negative when the contractive factors dominate over expansion factors. According to the curves in Figures 1 to 3, all of the combinations containing phenetole with Anilines (1^0, 2^0 &3^0) were dominated by the components that cause volume expansion &contraction. Further, V^E data of the aniline suggests that stronger interactions than N-methylaniline and N,N-dimethylaniline due to hydrogen bonding strength also [16]. It can be seen from Table 3, the more negative V^E = -0.586 $cm^3.mol^{-1}$at x_1=0.5199 was observed in phenetole + aniline when compared to V^E = -0.152 $cm^3.mol^{-1}$at x_1= 0.5624 in phenetole + N-methylaniline and V^E =0.020 cm^3 $.mol^{-1}$ at x_1= 0.5006 in phenetole + N,N-dimethylaniline systems at 303.15 K.

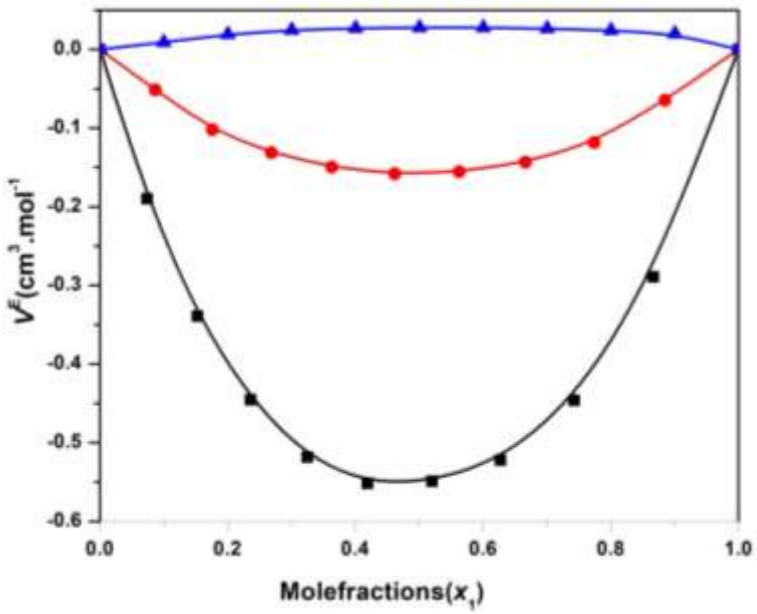

Figure 1: Variation of excess molar volume (V^E) with mole fraction (x_1) of Phenetole for the binary liquid mixtures of Phenetole with Aniline (■); N-Methylaniline (●); and N,N-dimethylaniline (▲) at 303.15 K

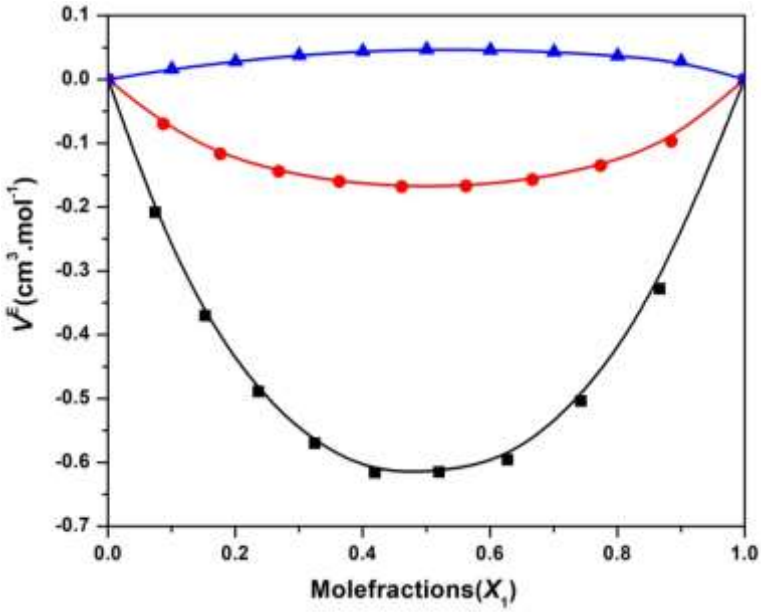

Figure 2: Variation of excess molar volume (V^E) with mole fraction (x_1) of Phenetole for the binary liquid mixtures of Phenetole with Aniline (■); N-Methylaniline (●); and N,N-dimethylaniline (▲) at 308.15 K

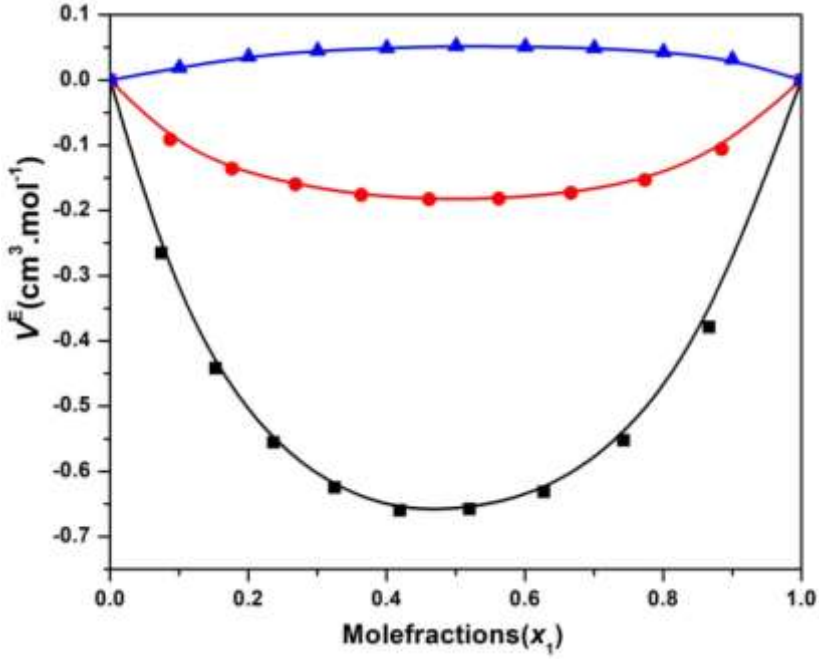

Figure 3: Variation of excess molar volume (V^E) with mole fraction (x_1) of Phenetole for the binary liquid mixtures of Phenetole with Aniline (■); N-Methylaniline (●); and N,N-dimethylaniline (▲) at 313.15 K

The V^E data of liquid mixtures following in the order:

Phenetole + Aniline >Phenetole + N-methyl Aniline >Phenetole + N,N-dimethyl Aniline

The results of the thermodynamic parameters of the above said liquids study that the solvent-solute interaction increases with the strength of base, the dissociation constants (P^K) of alkyl substituted aryl amines are: aniline (P^{Kb} = 9.38), N-methylaniline (P^{Kb} =9.16), N,N-dimethylaniline (P^{Kb} =8.32) K. From Fig. 1, the 1^0 - amines exhibited more intermolecular interaction than in 2^0- amines due to formation of hydrogen bond but Tertiary amines (N,N-dimethylaniline) do not exhibit intermolecular interaction due to the absence of H- atom. This result was confirmed by the FT-IR spectra. The responsible of negative sign and magnitude of V^E data in the binary liquid mixtures indicated due to the inductive effect and net packing effect. The temperature for all the three systems increases with increase of magnitude of V^E values. This is due to less thermal de-clustering of self-association than cross association of component molecules of mixture and lesser fitting of voids of one component molecule into another.

3.2. Excess isentropic compressibilities (κ_s^E)

The binary systems of Phenetole with anilines, speed of sound (u), isentropic compressibility (κ_s) and excess isentropic compressibility (κ_s^E) were reported in Table 4 at T= (303.15 and 313.15) K. The κ_s^E data of all the measured systems were graphically represented in Figures 4 and 5. The following equation was used to calculate the isentropic compressibility (κ_s) using the experimental density (ρ) and speed of sound (u) data.

Table 4: Molefraction (x_1) of Phenetole experimental sound speed (u), isentropic compressibilities (κ_s), excess isentropic compressibilities (κ_s^E) and predicted excess isentropic compressibilities (Redlich-Kister) theoretical sound speed values of Phenetole (1) with Aniline, N-Methylaniline and N,N-dimethylaniline (2) at 303.15K and 313.15 K and 0.1M Pa pressure.

x_1	u(exp) ($m.s^{-1}$)	κ_s (TPa^{-1})	U_{CFT}	U_{FLT}	U_{NOMOTO}	$\kappa_s^E/(TPa^{-1})$	
			($m.s^{-1}$)			Exp.	Redlich-Kister
Phenetole(1)+ Aniline(2)							
T=303.15 K							
0.0743	1595.69	389.22	1595.28	1609.23	1587.26	-9.97	-10.25

0.1529	1576.70	400.35	1573.86	1597.36	1559.30	-19.50	-19.04
0.2363	1555.06	413.55	1551.21	1580.06	1531.68	-26.73	-26.22
0.3249	1531.12	428.82	1527.25	1558.51	1504.41	-31.64	-31.56
0.4193	1506.11	445.69	1501.84	1532.76	1477.47	-34.72	-34.78
0.5199	1478.13	465.54	1474.87	1503.29	1450.90	-34.56	-35.49
0.6275	1450.35	486.58	1446.18	1471.76	1424.66	-32.93	-33.22
0.7428	1420.25	510.84	1415.59	1436.49	1398.76	-27.81	-27.26
0.8666	1385.31	540.89	1382.93	1395.90	1373.20	-16.61	-16.66
T=313.15K							
0.0743	1565.73	407.3	1559.67	1577.61	1551.42	-14.20	-14.18
0.1529	1546.39	419.3	1537.95	1566.27	1522.98	-24.85	-24.95
0.2363	1524.16	433.7	1515.00	1547.92	1494.91	-32.82	-32.68
0.3249	1498.83	450.9	1490.70	1525.05	1467.22	-37.80	-37.73
0.4193	1471.91	470.2	1464.92	1498.47	1439.88	-40.40	-40.39
0.5199	1443.42	492.0	1437.56	1468.61	1412.93	-40.34	-40.79
0.6275	1415.03	515.2	1408.41	1436.64	1386.33	-38.59	-38.67
0.7428	1385.10	541.4	1377.34	1401.04	1360.08	-33.62	-33.04
0.8666	1349.71	574.5	1344.18	1359.95	1334.21	-21.47	-21.63
Phenetole+ N-methylaniline (2)							
T=303.15 K							
0.0869	1532.38	434.8	1531.46	1537.41	1528.31	-4.78	-4.76
0.1764	1514.20	446.3	1513.11	1525.18	1507.46	-8.49	-8.62
0.2686	1496.04	458.3	1494.27	1511.08	1486.81	-11.67	-11.64
0.3635	1477.38	471.1	1474.97	1496.15	1466.38	-14.01	-13.81

0.4614	1457.96	485.1	1455.15	1480.16	1446.14	-15.26	-15.10
0.5624	1437.48	500.4	1434.81	1463.46	1426.10	-15.14	-15.38
0.6666	1417.04	516.4	1413.94	1445.99	1406.26	-14.30	-14.44
0.7741	1395.79	533.8	1392.53	1427.50	1386.64	-12.02	-11.93
0.8852	1372.78	553.6	1370.54	1407.39	1367.20	-7.36	-7.36
T=313.15K							
0.0869	1496.60	460.6	1493.68	1498.37	1490.63	-6.61	-6.63
0.1764	1478.74	472.8	1475.05	1481.34	1469.60	-11.07	-11.11
0.2686	1459.51	486.5	1455.97	1462.53	1448.77	-14.04	-13.99
0.3635	1439.58	501.2	1436.45	1443.12	1428.17	-15.91	-15.76
0.4614	1419.49	516.8	1416.44	1422.96	1407.76	-16.96	-16.72
0.5624	1398.95	533.5	1395.92	1402.16	1387.54	-16.92	-16.98
0.6666	1378.59	550.8	1374.91	1380.81	1367.52	-16.21	-16.33
0.7741	1357.26	569.7	1353.38	1358.86	1347.71	-13.82	-14.16
0.8852	1334.97	590.6	1331.31	1335.28	1328.10	-9.49	-9.33
Phenetole+ N,N-dimethylaniline(2)							
T=303.15 K							
0.1002	1457.07	496.42	1457.84	1457.43	1457.75	-0.92	-0.96
0.2004	1444.25	504.93	1445.39	1444.38	1445.24	-1.76	-1.70
0.3005	1431.53	513.57	1433.01	1431.81	1432.81	-2.32	-2.26
0.4006	1419.02	522.28	1420.68	1419.36	1420.45	-2.66	-2.64
0.5006	1406.80	531.00	1408.41	1407.03	1408.18	-2.83	-2.84
0.6006	1394.75	539.80	1396.20	1394.90	1395.98	-2.77	-2.84
0.7005	1383.00	548.59	1384.06	1382.72	1383.86	-2.57	-2.63

0.8004	1371.35	557.52	1371.96	1370.74	1371.81	-2.09	-2.08
0.9002	1359.76	566.62	1359.94	1358.87	1359.85	-1.29	-1.28
T=313.15K							
0.1002	1419.35	527.90	1419.97	1418.96	1416.27	-1.43	-1.46
0.2004	1406.35	537.37	1407.37	1405.52	1401.02	-2.25	-2.26
0.3005	1393.46	546.98	1394.84	1392.53	1386.80	-2.75	-2.69
0.4006	1380.80	556.66	1382.36	1379.88	1373.48	-3.07	-2.94
0.5006	1368.44	566.34	1369.94	1367.37	1360.99	-3.22	-3.13
0.6006	1356.33	576.07	1357.58	1355.03	1349.27	-3.19	-3.25
0.7005	1344.51	585.79	1345.28	1342.81	1338.22	-3.03	-3.22
0.8004	1332.97	595.51	1333.02	1330.84	1327.82	-2.75	-2.82
0.9002	1321.31	605.56	1320.83	1319.21	1317.98	-1.98	-1.91

The standard uncertainties are u(x) ± $1x10^{-4}$, u(u) = 0.5 $m.s^{-1}$, u(T) = 0.02 K and u(p) = ±$5x10^{-5}$g cm^{-3}. Uc(K_S^E) =0.03TPa^{-1}

$$\kappa_s = \frac{1}{u^2 \rho} \quad (3)$$

and the κ_s^E were estimated by adopting the following equation:

$$\kappa_s^E = \kappa_s - \kappa_s^{id} \quad (4)$$

Where, κ_s^{id} represents the ideal value of the isentropic compressibility which was calculated from the Benson and Kiyohara equation [32].

$$\kappa_s^{id} = \sum_{i=1}^{2} \phi_i \left[\kappa_{s,i} + TV_i \left(\alpha_i^2 \right) / C_{p,i} \right] - \left\{ T \left(\sum_{i=1}^{2} x_i V_i \right) \left(\sum_{i=1}^{2} \phi_i \alpha_i \right)^2 / \sum_{i=1}^{2} x_i C_{p,i} \right\} \quad (5)$$

where, C_{pi} and α_i are the molar heat capacity and the thermal expansion coefficient of the i^{th} component respectively. The $C_{p,i}$ values were collected from literature [15,16].

The chemical and physical interactions of binary liquid mixtures for κ_s^E data were explained our previous studies. [1]. The increase in κ_s^E magnitude with temperature may be caused by the aromatic amines increased free volume as a result of accommodating the ether molecule. In addition to these interactions, negative κ_s^E data may also be caused by the component molecules different sizes and shapes, which may allow them to fit into one another's structures and reduce volume and compressibility. This would produce a negative deviation from Table 4 in compressibility. Further, it is concluded that, as the temperature rises in binary mixtures as shown in Figures 4 and 5, the negative κ_s^E value shifts from aniline to N,N-dimethylaniline.

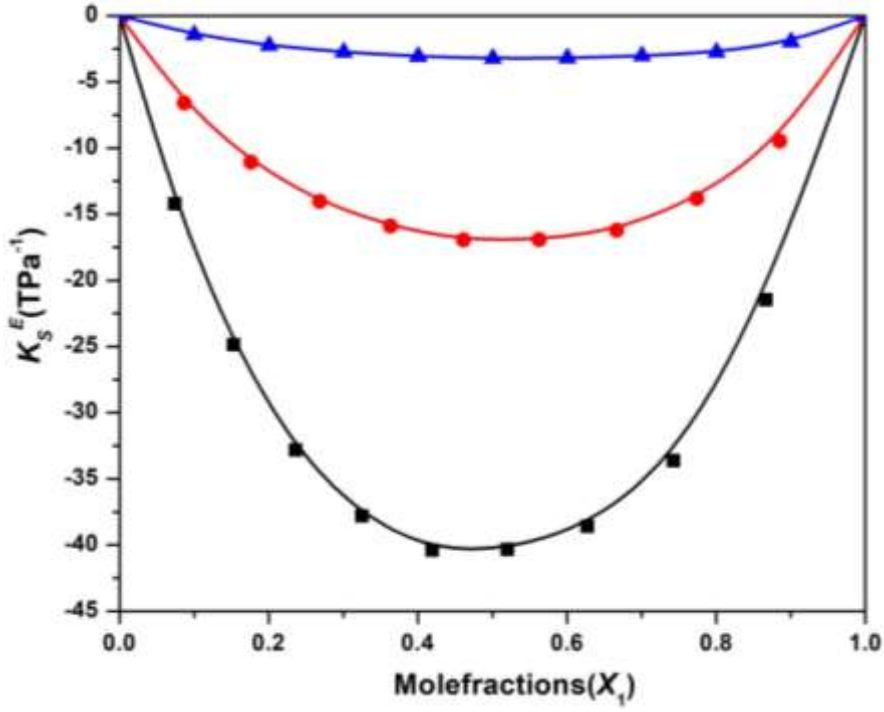

Figure 4: Excess isentropic compressibility (κ_s^E) with mole fraction (x_1) of Phenetole for the binary liquid mixtures of Phenetole with Aniline (■); N-Methylaniline (●); and N,N-dimethylaniline (▲) at 303.15 K

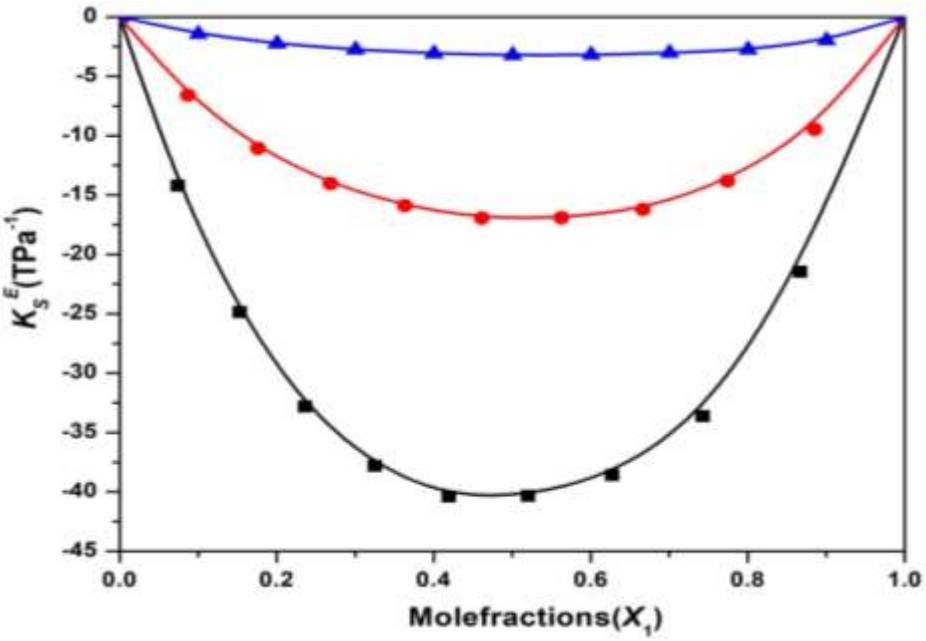

Figure 5: Excess isentropic compressibility (κ_s^E) with mole fraction (x_1 of Phenetole for the binary liquid mixtures of Phenetole with Aniline (■); N-Methylaniline (●); and N,N-dimethylaniline (▲) at 313.15 K

The binary liquid mixes of phenetole and aromatic amines exhibit the following order of negative algebraic values for κ_s^E are,

Phenetole +aniline>Phenetole + N- methylaniline>Phenetole+ N,N-dimethylaniline

Due to the dissociation of the associated structure between phenetole and aniline mixture, which forms stronger O---H bonds than the other phenetole with N- methylaniline and N,N- dimethylaniline, the values of κ_S^E become more negative as the strength of interactions between component molecules increases. By releasing free phenetole, we hypothesize that pure phenetole would disrupt the self-association of aromatic amines by mixing N-methylaniline and N,N- dimethylaniline through hydrogen bonds to form complex structures. The interactions that occur as a result of the interstitial accommodation and/or cross-association between the hydrogen atom of the aniline molecule and the oxygen atom of the ether. Additionally, the OC_2H_5 and –N groups in N,N- dimethylaniline were dissimilar in the Phenetole + N,N- dimethylaniline system, preventing the formation of intermolecular hydrogen bonds and resulting in less negative κ_S^E. Finally, the mixture's predominant H-bonding interactions can be seen in the negative V^E and κ_S^E values across the entire mole fraction of Phenetole with aromatic amines.

From Table 5, the experimental speed of sound data were compared with theoretical values of Collision factor Theory (CFT) [33], Free length theory (FLT) [34, 35], Nomoto's

relation [36]. The theoretical model proposed by Schaff's CFT gives good experimental results of speed of sound data than the other two models.

Table 5: RMSD of speed of sound (u) of Phenetole (1) with Aniline, N-methylaniline, N,N-dimethylaniline (2) at T= ,303.15 K, 313.15K from CFT, FLT and Nomoto models.

RMSD (Temperature)	CFT	FLT	Nomoto
Phenetole (1)+ Aniline (2)			
303.15K	0.0021	0.0129	0.0135
313.15K	0.0045	0.0129	0.0163
Phenetole(1)+ N-methylaniline (2)			
303.15K	0.0015	0.0173	0.0058
313.15K	0.0077	0.0017	0.0282
Phenetole(1)+ N,N-dimethylaniline(2)			
303.15K	0.0026	0.0003	0.0022
313.15K	0.0007	0.0009	0.0039

The merits of these three theories were compared in terms of relative root mean deviation (RMSD) by using the given following equation:

$$\text{RMSD} = \left[\frac{1}{n}\sum_{i=1}^{n}\left[\frac{y_{exp}-y_{cal}}{y_{exp}}\right]^2\right]^{1/2} \qquad (6)$$

In the present study, Schaff's CFT model gives good estimation in speed of sound for all the binary liquid mixtures of RMSD.

From, Table 6, the least-square fitting values of parameters was obtainedfrom Redlich – kister [37] equation of phenetole with aromatic amines.

Table 6: Standard deviation σ (V^E) and σ (κ_s^E) values of constants (a_0, a_1, a_2; b_0, b_1, b_2) for Redlich-Kister, Eq. (2) et al. for Phenetole(1) with Aniline, N-methylaniline and N,N-dimethylaniline.

Temperature	Function	Redlich-Kister			
		a_0	a_1	a_2	σ
Phenetole(1) +Aniline (2)					
303.15K	V^E ($cm^3.mol^{-1}$)	-2.2284	0.1048	-0.6382	0.003

308.15K	V^E ($cm^3.mol^{-1}$)	-2.4959	-0.1303	-1.0053	0.003
313.15K	V^E ($cm^3.mol^{-1}$)	-2.6336	0.1542	-0.6889	0.003
303.15K	κ_s^E (TPa^{-1})	-142.27662	2.3203	-6.5092	0.5487
313.15K	κ_s^E (TPa^{-1})	-163.5883	5.8894	-51.8550	0.3168
Phenetole(1) + N-methylaniline (2)					
303.15K	V^E ($cm^3.mol^{-1}$)	-0.6497	0.0109	-0.0162	0.003
308.15K	V^E ($cm^3.mol^{-1}$)	-0.6649	-0.0419	-0.3876	0.003
313.15K	V^E ($cm^3.mol^{-1}$)	-0.7155	0.0110	-0.5731	0.003
303.15K	κ_s^E (TPa^{-1})	-61.345797	-8.2375	-7.9198	0.1665
313.15K	κ_s^E (TPa^{-1})	-67.6375	-6.9270	-31.7551	0.2008
Phenetole(1) + N,N-dimethylaniline (2)					
303.15K	V^E ($cm^3.mol^{-1}$)	0.1095	0.0500	0.0767	0.003
308.15K	V^E ($cm^3.mol^{-1}$)	0.1809	0.0635	0.0898	0.003
313.15K	V^E ($cm^3.mol^{-1}$)	0.2044	0.0634	0.1219	0.003
303.15K	κ_s^E (TPa^{-1})	-11.3617	-2.0443	-1.6556	0.0517
313.15K	κ_s^E (TPa^{-1})	-12.4963	-3.1659	-9.7193	0.1152

The corresponding standard deviations $\sigma(Y^E)$ are estimated by the given following formula

$$\sigma(Y^E) = [\Sigma(Y^E_{exp} - Y^E_{cal})^2/(m-n)]^{1/2} \quad (7)$$

where $\sigma(Y^E)$ is V^E/κ_S^E. 'm' is the total number of experimental points and 'n' is the number of coefficients.

3.3. Experimental details of FT-IR studies:

FT-IR spectra changes are broadly utilized in investigation of intermolecular H-bonding presence between the binary liquid mixtures of phenetole and aniline, N-methylaniline, N,N-dimethylaniline. The spectroscopic studies used for the formation of strong hydrogen-bonding between C-O-C stretching of phenetole and -NH stretching of aniline, N-methylaniline. However, compared to the other liquid mixturescontainingphenetole withN,N-dimethylaniline hada weaker solute-solvent interactions. The values of vibration frequencies and spectra's were included in Table 7 and Figs. 6, 7 and 8.

Table 7: Experimental FT-IR Frequencies with wavenumbers (cm^{-1}) and Shifting of bands of Phenetole (1) + Aniline, N-methylaniline and N,N-dimethylaniline (2) binary mixtures at 298.15K.

Compound	Band	Experimental
		$\nu(c.m^{-1})$
Phenetole	C-O-C	1235.23 (Asym) and 1043.46 (Sym)
Aniline	$-NH_2{}^a$	3433.05 (w) and 3356.09 (m)
N-MethylAniline	$-NH^b$	3412.38 (m)
N,N-DiMethylAniline	$-N^c$	No peak
Phenetole+ Aniline	$-NH_2{}^d$	3467.27 (w) and 3372.18 (m)
Phenetole +N-Methyl Aniline	$-NH^e$	3417.60 (m)
Phenetole +N,N-Di Methyl Aniline	$-N^f$	No peak
Shift in wavenumbers with respect to Aromatic anilines values		$\delta\nu(c.m^{-1})$
Phenetole+ Aniline	$-NH_2{}^d$--$NH_2{}^a$	34.22 (w) and 16.09 (m)
Phenetole +N-Methyl Aniline	$-NH^e$--NH^b	5.22
Phenetole +N,N-Di Methyl Aniline	$-N^c$--N^f	No peak

Furthermore, an examination of FT-IR spectral data for the equimolar binary liquid mixtures have Hydrogen bonding interaction between amine and ether functional groups (except N,N-dimethylaniline).This band (hydrogen bonded –O- stretching) can be seen in the pure liquids [37]. An amine functional group and phenetole exhibit band –O− stretching at 1235.23cm^{-1}(ASym) and 1043.46 cm^{-1}(Sym) in the experimental FT-IR spectrum of the pure components' absorption bands: aniline (two peaks at 3433.05 cm^{-1}(w), 3356.09 cm^{-1}(m)), N-methylaniline (one peak at 3412.38 cm^{-1}(m)), and N,N-dimethylaniline (no peak). In addition, the absorption bands of binary liquid frequencies are as follows: phenetole + aniline = 3467.27 cm^{-1}(w) and 3372.18cm^{-1}; phenetole + N-methylaniline = 3417.60 cm^{-1}(m) and phenetole + N,N-dimethylaniline = no peak, as indicated in Table- 7 and depicted in the figures. 6, 7 and 8.

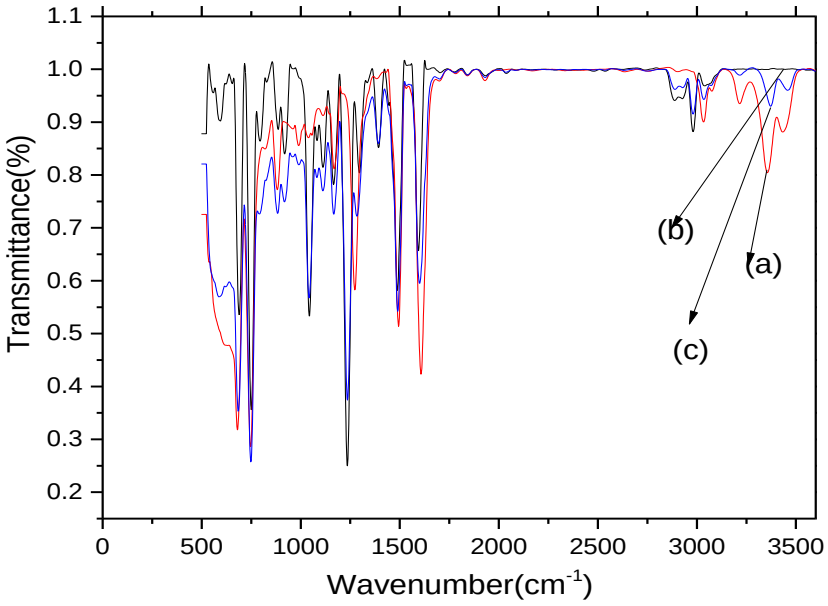

Figure 6: Normalized FT-IR Spectra of (Phenetole + Aniline) binary mixture over the range (3500- 1000 cm^{-1}). peak a: Phenetole (P); peak b: Aniline (A); peak c: Phenetole with Aniline (P+A).

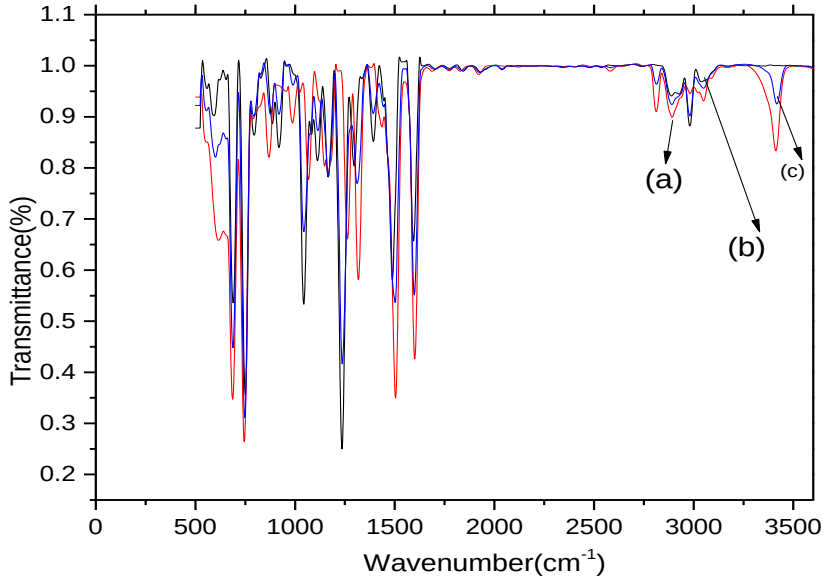

Figure 7: Normalized FT-IR Spectra of (Phenetole + N-Methylaniline) binary mixture over the range (3500- 1000 cm^{-1}). peak a: Phenetole (P); peak b: N-Methylaniline (NMA); peak c: Phenetole with N-Methylaniline (P+NMA).

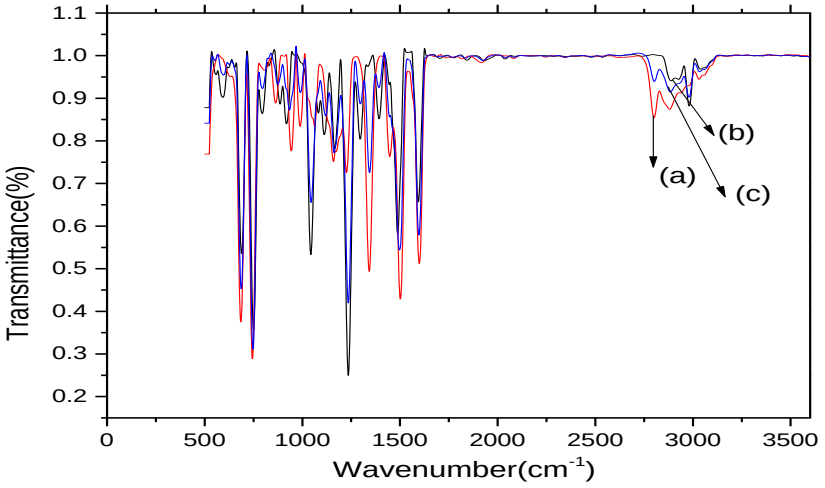

Figure 8: Normalized FT-IR Spectra of (Phenetole + N,N-dimethylaniline) binary mixture over the range (3500- 1000 cm^{-1}). peak a: Phenetole (P); peak b: N,N-dimethylaniline (NNDMA); peak c: Phenetole with N,N-dimethylaniline (P+NNDMA).

The experimental results from FT-IR spectroscopy suggest that because the –O···H-N− band is longer, there is a strong hydrogen bond between phenetole and aniline, shifting the band to a higher frequency. In aromatic primary amines these absorptions are usually 15 to 40 cm^{-1} higher in frequency.The –O···H-N− band is shifted to a lower frequency change in the binary systems of phenetole and N-methylaniline due to weak H-bonding.However, no N-H absorptions of phenetole with N,N-dimethylaniline.From the above FT-IR Spectral analysis results said that the binary liquid mixtures were fallows below systematic order:

Phenetole +aniline>Phenetole + N-methylaniline>Phenetole+ N,N-dimethylaniline

Finally, concluded that experimental FT-IR Spectroscopy analysis concur with those of the experimental, theoretical studies.

4. Conclusions:

The binary mixtures ofPhenetole with substituted aniline (Aniline, N-methylaniline and N,N-dimethylaniline) of densities and speeds of the sound were measured at different temperatures and their excess molar volumes (V^E) and excess isentropic compressibilities (κ_S^E) values were also calculated. Except for the system containing N,N-dimethylaniline, all binary mixes have negative V^E values. The negative results show that hydrogen bonds and dipole-dipole interactions between the constituents strongly attract one another. The FT-IR spectra analysis further supported the existence of intermolecular hydrogen bonding interactions. The analysis of hydrogen bonding interaction between Phenetole with aniline and N-methylaniline (with the exception of N,N-dimethylaniline) can be concluded from thermophysical properties and spectroscopic studies.

Declaration of Competing Interest

The authors declare that they is no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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