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Molecular Interaction Studies on Aniline Containing Organic Liquid Mixtures Using Ultrasonic Technique

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Abstract: Density, viscosity and ultrasonic velocity have been measured for four ternary liquid mixtures containing aniline + benzene with cyclohexane and n-heptane, aniline + toluene with cyclohexane and n-heptane at temperature 303 K. The adiabatic compressibility, free length, free volume, internal pressure and their excess values have been calculated from the experimental data. These parameters are used to discuss the molecular interactions between the component molecules and the excess functions are found to be sensitive to the nature and extent of the interactions taking place in these ternary mixtures.

Key words: Ternary systems · Ultrasonic velocity · Acoustical parameters · Molecular interactions

INTRODUCTION

The dielectric [1, 2] and ultrasonic studies [3, 4] have provided enormous data in precisely understanding the molecular interactions and structural behavior of molecules and their mixtures. In this paper, we report on the ultrasonic study of four ternary liquid mixtures. Ultrasonic waves have been used by many scientists to investigate the nature of molecular interactions and physico-chemical behavior of pure, binary and ternary liquid mixtures [5, 6]. Mixed solvent rather than single pure liquids are of utmost practical importance in most chemical and industrial processes as they provide a wide range of mixtures of two or more components in varying proportions so as to permit continuous adjustment of desired properties of the medium. Ultrasonic velocity together with density and viscosity data furnish wealth of information about the interaction between ions, dipoles, hydrogen bonding, multipolar and dispersive forces [7, 8].

The cyclohexane and n-heptane are non-polar, unassociated, inert hydrocarbons and cyclohexane possesses globular structure [9]. Alkanes have been studied extensively in view of their importance in petrochemical industries, particularly in the light of the present day trends towards heavier feedstock. Aniline molecule is highly polar and self associated through hydrogen bonding of their amine group. It is used in the manufacturing of synthetic dyes, drugs and as an accelerator in vulcanization of rubber. Benzene is a non-polar solvent, which can freely miscible with many organic solvents [10] and toluene, which is aprotic and polar in nature due to the presence of electron releasing methyl group. It is used as an octane booster in fuel, as a solvent for many organic compounds, paints, cleaning of polymer surface and electronic materials, as a raw material for toluene diisocyanate which is used for manufacturing the polyurethane, foams etc., the present study thus deals with the measurement of density, viscosity and ultrasonic velocity for ternary system formed by aniline + benzene with cyclohexane and n-heptane, aniline + toluene with cyclohexane and n-heptane. From the measured data, the adiabatic compressibility, free length, free volume, internal pressure and their excess values were calculated. The variations of these parameters with composition of the mixtures are discussed in terms of molecular interactions.

EXPERIMENTAL DETAILS

The ultrasonic velocity for the mixtures was measured using the ultrasonic interferometer (Mittal Enterprises, New Delhi) at fixed frequency of 3 MHz with an accuracy of ±0.1%. The density and viscosity are measured using specific gravity bottle and an Ostwald's viscometer respectively.

The mixtures of various concentrations in mole fraction are prepared by taking purified AR grade samples at 303 K. In the mixtures, the mole fraction of the second component, benzene (in systems I and II) and

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toluene (in systems III and IV) was kept fixed (0.3), while the mole fraction of the remaining two were varied from 0.0 to 0.7 so as to have the mixtures of different compositions.

Using the measured data, the acoustic parameters, such as adiabatic compressibility(β), free length(L_f), free volume(V_f) and internal pressure π_i) and their excess parameters have been calculated using the following expressions

$$\beta = \frac{1}{\rho U^2} \quad (1)$$

$$L_f = K_T \beta^{1/2} \quad (2)$$

$$V_f = \left[\frac{M_{eff} U}{K\eta}\right]^{3/2} \quad (3)$$

$$\pi_i = bRT\left[\frac{K\eta}{U}\right]^{1/2}\left[\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right] \quad (4)$$

$$A^E = A_{exp} - A_{id} \quad (5)$$

and

$$A_{id} = \sum_{i=1}^{n} A_i X_i \quad (6)$$

where the notations have their usual meaning.

RESULTS

Table 1 gives the measured values of density, viscosity and ultrasonic velocity of the pure liquids and same for the four ternary systems are listed in Table 2. Table 3 shows the values of adiabatic compressibility, free length, free volume and internal pressure for all the pure liquids and the Table 4 summarizes the same for ternary liquid mixtures. Excess values of these parameters are given in Table 5.

Table 1: Values of density (ρ), viscosity (η) and velocity (u) of pure liquids

Liquids	ρ kg m^{-3}	η X 10^3 N s m^{-2}	U m s^{-1}
Aniline	1017.0	2.9510	1614.5
Benzene	867.8	0.5712	1295.2
Toluene	857.8	0.5260	1287.2
Cyclohexane	767.7	0.8003	1230.3
n-heptane	667.1	0.3060	1121.0

Table 2: Values of density (ρ), viscosity (η) and velocity (u) of system I,II,III and IV at 303 K

Mole Fraction				
X_1	X_3	ρ kg m^{-3}	η x 10^3 N s m^{-2}	U m s^{-1}
aniline + benzene + cyclohexane				
0.0000	0.7001	782.76	0.5763	1208.4
0.1001	0.5999	805.60	0.6202	1245.0
0.2001	0.4999	833.69	0.6917	1272.0
0.2999	0.4001	852.64	0.7799	1306.2
0.4000	0.3002	884.63	0.8952	1338.6
0.5003	0.2002	913.36	1.0509	1386.0
0.6001	0.1000	940.91	1.2551	1442.7
0.6999	0.0000	967.74	1.5262	1506.3
aniline + benzene + n-heptane				
0.0000	0.6999	710.71	0.3715	1130.4
0.1002	0.5998	738.26	0.4175	1158.6
0.1999	0.4999	770.62	0.5042	1205.4
0.3000	0.4002	800.62	0.5752	1220.7
0.4000	0.3002	832.52	0.7187	1263.0
0.4996	0.1999	877.56	0.8642	1336.8
0.5999	0.0998	921.15	1.0883	1489.5

Table 2: Continued

aniline + toluene + cyclohexane				
0.0000	0.6664	787.84	0.5811	1235.4
0.1000	0.6000	807.87	0.6400	1248.0
0.2004	0.4992	833.51	0.6729	1275.9
0.3001	0.3999	851.28	0.7582	1301.4
0.4003	0.2999	877.19	0.8874	1348.8
0.5000	0.2001	904.21	1.0154	1388.7
0.6002	0.0999	933.21	1.1987	1440.3
0.6998	0.0000	954.59	1.3986	1489.5
aniline + toluene + n-heptane				
0.0000	0.6671	718.59	0.3872	1129.2
0.1000	0.6002	741.07	0.4247	1170.6
0.2002	0.4996	772.97	0.4864	1198.5
0.2999	0.4000	801.61	0.5607	1233.6
0.4002	0.2999	835.23	0.6892	1274.4
0.5002	0.1998	877.92	0.8547	1335.3
0.6001	0.0998	926.22	1.0556	1410.0
0.6998	0.0000	954.59	1.3986	1489.0

Table 3: Values of adiabatic compressibility(β),free length(L_f), free volume(V_f) and internal pressure(π_i) of pure liquids

Liquids	β x 10^{10} Pa^{-1}	L_f x 10^{10} m	V_f x 10^7 m^3 mol^{-1}	π_i x 10^{-6} Pa
Aniline	3.7722	0.3875	0.4107	717.96
Benzene	6.8691	0.5229	2.6625	389.97
Toluene	7.0359	0.5292	3.8238	306.87
Cyclohexane	8.6057	0.5853	1.6619	399.63
n-heptane	11.9288	0.6891	7.9437	191.36

Table 4: Values of adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) of system I,II,III and IV

Mole fraction					
X_1	X_3	β x 10^{10} Pa^{-1}	L_f x 10^{10} m	V_f x 10^7 m^3 mol^{-1}	π_i x 10^{-6} Pa
aniline + benzene + cyclohexane					
0.0000	0.7001	8.7488	0.5902	2.5625	355.55
0.1001	0.5999	8.0083	0.5647	2.4397	365.77
0.2001	0.4999	7.4135	0.5433	2.1737	386.12
0.2999	0.4001	6.8741	0.5231	1.9196	405.66
0.4000	0.3002	6.3087	0.5012	1.6451	434.64
0.5003	0.2002	5.6994	0.4764	1.3841	467.08
0.6001	0.1000	5.1062	0.4509	1.1437	504.24
0.6999	0.0000	4.5543	0.4258	0.9239	547.93
aniline + benzene + n-heptane					
0.0000	0.6999	11.0110	0.6621	5.4267	238.40
0.1000	0.5998	10.4819	0.6459	4.6730	259.38
0.1999	0.4999	8.9309	0.5963	3.6939	288.95
0.3000	0.4002	8.3822	0.5777	3.0539	317.44
0.4000	0.3002	7.5301	0.5475	2.2745	362.81
0.4998	0.1999	6.3766	0.5039	1.8565	402.53
0.5999	0.0998	5.4651	0.4665	1.4054	458.58

Table 4: Continued

aniline + toluene + cyclohexane					
0.0000	0.6664	8.3166	0.5754	2.8190	334.61
0.1000	0.6001	7.9475	0.5625	2.5150	351.03
0.2004	0.4992	7.3698	0.5417	2.4487	359.18
0.3001	0.3999	6.9359	0.5255	2.1412	378.37
0.4003	0.2999	6.2664	0.4995	1.8112	405.44
0.5000	0.2001	5.7347	0.4778	1.5690	431.15
0.6002	0.0999	5.1655	0.4535	1.3112	464.42
0.6998	0.0000	4.7217	0.4336	1.1102	495.16
aniline + toluene + n-heptane					
0.0000	0.6671	10.9140	0.6592	5.4390	233.04
0.1000	0.6002	9.8474	0.6261	4.9434	246.77
0.2002	0.4996	9.0066	0.5988	4.1327	270.73
0.2999	0.4000	8.1976	0.5713	3.4485	296.08
0.4002	0.2999	7.3720	0.5418	2.6276	334.82
0.5002	0.1998	6.3883	0.5043	2.0179	379.86
0.6001	0.0999	5.4306	0.4649	1.5773	429.51

Table 5: Excess values of adiabatic compressibility (β^E), free length (L_f^E), free volume (V_f^E) and internal pressure (π_i^E) of system I, II, III and IV

Mole fraction					
X_1	X_3	β^E x 10^{10} Pa^{-1}	L_f^E x 10^{10} m	V_f^E x 10^7 m^3 mol^{-1}	π_i^E x 10^{-6} Pa
aniline + benzene + cyclohexane					
0.0000	0.7001	0.6638	0.0236	0.6005	-41.1765
0.1001	0.5999	0.4074	0.0179	0.6029	-54.1491
0.2001	0.4999	0.2960	0.0163	0.4620	-74.3042
0.2999	0.4001	0.2391	0.0158	0.3329	-86.5505
0.4000	0.3002	0.1571	0.0137	0.1837	-89.4275
0.5003	0.2002	0.0305	0.0086	0.0476	-88.9609
0.6001	0.1000	-0.0781	0.0031	-0.0674	-83.5225
0.6999	0.0000	-0.1472	0.0023	-0.1625	-71.6004
aniline + benzene + n-heptane					
0.0000	0.6999	1.4174	0.0531	-0.1778	104.5948
0.1002	0.5996	1.7027	0.0669	-0.1791	62.0804
0.1999	0.4999	0.9660	0.0474	-0.4066	29.8656
0.3000	0.4002	1.2329	0.0591	-0.2993	-3.2237
0.4000	0.3002	1.1975	0.0590	-0.3181	-26.8962
0.4998	0.1999	0.8605	0.0463	0.0178	-47.1266
0.5999	0.0998	0.7637	0.0383	0.3190	-62.6897
aniline + toluene + cyclohexane					
0.0000	0.6664	0.1820	0.0089	0.4363	104.7452
0.1000	0.6000	0.2970	0.0138	0.3300	72.3750
0.2004	0.4992	0.2043	0.0129	0.3882	27.6145
0.3000	0.3999	0.2515	0.0165	0.2066	-5.6242
0.4003	0.2999	0.0661	0.0102	0.0021	-31.3078
0.5000	0.2001	0.0167	0.0083	-0.1153	-58.1211
0.6002	0.0999	-0.0682	0.0038	-0.2477	-77.3782
0.6998	0.0000	-0.0033	0.0035	-0.3245	-99.3295

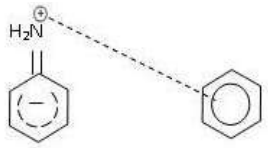
Table 5: Continued

aniline + toluene + n-heptane					
0.0000	0.6671	3.7544	0.0482	0.5159	-45.6220
0.1000	0.6002	1.0204	0.0453	-0.2553	-84.7060
0.2002	0.4996	0.9924	0.0481	0.3152	-113.2280
0.2999	0.4000	1.0006	0.0508	-0.2448	-140.6700
0.4002	0.2999	0.9912	0.0515	-0.3119	-154.5890
0.5002	0.1998	0.8225	0.0441	-0.1688	-162.1860
0.6001	0.0998	0.6785	0.0348	0.1418	-165.0220

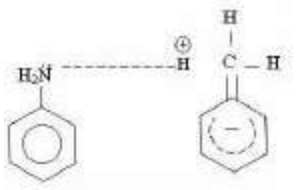
DISCUSSION

It is evident from the Table 2 that in all the systems, the density, viscosity and ultrasonic velocity increase with increase in mole fraction of aniline. This behaviour is different from the ideal mixture and this can be attributed to the intermolecular interaction in the systems [11].

When benzene is added with aniline, dipole-induced dipole interaction arises between $\overset{\odot}{N}H_2$ and the loop of 6π electrons of benzene ring as given below:



When aniline is added with toluene, the same type of interaction exists between the lone pair electron on nitrogen and $\overset{\odot}{H}$ of the hyperconjugative structure of toluene. The probable interaction structure of aniline and toluene is depicted below:



From Table 2, it is understood that for the same mole fraction, on comparing the velocity values of the binary mixtures of aniline with benzene and aniline with toluene, the later one has low value which may be due to steric effect attributed by the methyl group of toluene. It is also observed that the velocity of the binary mixtures get decreased from their individual values. It is well known that cyclohexane and n-heptane are inert; the only reason for the decrease of velocity in the binary mixtures may be due to molecular dispersive forces existing between them.

The existence of electrostatic force between the interacting molecules changes the structure of the molecules. The structural changes affect the compressibility and hence there is a change in ultrasonic velocity.

As benzene is having relatively higher dielectric constant (ϵ=2.275) and being an electron donor than cyclohexane (ϵ = 2.02) and n-heptane (ϵ=1.92), the interaction between the molecules of benzene with cyclohexane and n-heptane is found to be weaker than the interaction with the aniline. In the case of binary mixtures of aniline with cyclohexane or n-heptane, only dispersive interactions exist between them is due to the non-polar nature and inertness. Similar type of interactions exists between toluene and cyclohexane.

The addition of aniline with the binary mixture of benzene and toluene with cyclohexane(or heptane) disturbs the structure due to the presence of dipole-induced dipole interactions. This contributes to a decrease in free length and hence compressibility. The regular fall in free length with the mole fraction of aniline may be attributed to the close approach of the molecules. According to Erying and Kincaid [12], the regular fall in free length causes a rise in sound velocity in the mixture. This is also in accordance with expected decrease in adiabatic compressibility following an increase in the sound velocity in all the mixtures studied. Further this trend is an indication of clustering together of the molecules into some cage like agglomerates due to associative effect of the polar group predominating over the other types of interactions [13].

It is observed from Table 3 that a decrease in free volume and increase in internal pressure with increase in concentration of aniline respectively, which may be attributed to the increase in magnitude of interaction. The decrease in free volume shows that the clustering is due to dipole-induced dipole interaction. It is primarily due to the formation of spherical cage-like structure owing to the closer packing of the molecule [14].

The sign of excess values play a vital role in assessing the compactness due to molecular rearrangement and the extent of molecular interactions in liquid mixtures. It can be seen from Table 5 that the excess adiabatic compressibility and excess free length are positive and decrease with increasing mole fraction of aniline and attain negative values. This indicates weak interaction due to dispersive forces [15].

It is evident that the addition of cyclohexane or n-heptane weakens the strength of interaction and the ternary mixture tends to approach ideal behavior, as reported by Rastogi [16]. In all the mixtures studied, the positive values of excess properties correspond mainly to the existence of dispersive force which indicates structure breaking tendency while negative value of β^E is associated with structure forming tendency. In the present investigation the deviation in β^E shows that weak interaction between the unlike molecules, which is in agreement with Shakila, [17].

The values of excess intermolecular free length are positive as expected, this suggests that, in addition to dipole-dipole and dipole-induced dipole interactions, dispersive forces are also operative in all the systems [18].

The positive values of excess free volume in all the four systems (Table 5) are due to the weakening of dipolar interaction between the molecules of the mixture. Such behaviour is also noticed by Ali *et al*. [19]. The negative excess internal pressure in all mixtures indicates weak interactions between component molecules [20, 21].

CONCLUSION

It is concluded from the experimental and calculated parameters that, in system I and II the density, viscosity and velocity increases with increase in mole fraction of aniline. This is due to the dipole-induced dipole interaction between $\overset{\odot}{N}H_2$ and the loop of 6π electrons of benzene ring. In systems III and IV, the density, viscosity and velocity increase with increase in mole fraction of aniline which is also due to dipole-induced dipole interactions existing between the lone pair of electron of nitrogen and $\overset{\odot}{H}$ of the hyperconjugative structures of toluene. In all the above four ternary mixtures, for the same mole fraction of (i) aniline with benzene and (ii) aniline with toluene, the velocity decreases in the later case which may be due to steric effect attributed with the methyl group of toluene. The observed positive excess values in all the mixture indicate the weak interactions between the unlike molecules.

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