Ultrasonic Studies on Excess Thermodynamic Properties of Ternary Liquid Mixtures of Amide with Ethyl Benzoate in Benzene at 303.15K

B. Nagarjun[1], R. Kumar[2], G.V. Rama Rao[3], Ch. Rambabu[4], A.V. Sarma[5]

[1]Department of Physics, G.V.P. College of Engineering(A), Visakhapatnam,

[2]Department of Physics, The New College, Chennai,

[3] Department of Physics D.A.R. College, Nuzvid,

[4]Department of Physics, Acharya Nagarjuna University, Guntur,

[5] Department of Physics, Andhra University, Visakhapatnam.

Abstract: *The ultrasonic velocities, densities and viscosities of ternary mixtures of N, N – dimethyl formamide and N, N – dimethyl acetamide with ethyl benzoate in non – polar solvent benzene have been measured over the whole range of compositions at 303.15 K and atmospheric pressure. The excess molar volumes (V^E), excess intermolecular free length (L_f^E), excess internal pressure (π_i^E) excess free volume V_f^E) along with deviation in isentropic compressibility ($\Delta\beta_{ad}$) and deviation in viscosity($\Delta\eta$) have been calculated for these mixtures. The variation of these excess parameters with composition reveals the non ideal behavior of these ternary systems. The sign and magnitude of these excess parameters identifies the existence of strong intermolecular interactions between the aliphatic and aromatic components in these mixtures.*

1. Introduction

A thorough knowledge of thermodynamic and transport properties of multi-component systems is essential in many industrial applications such as design calculation, absorption heat pumps, heat transfer, mass transfer and fluid flow. Besides, the derived properties, in combination with other mixing properties, provide valuable information as much for qualitatively analyzing the molecular interactions and for understanding structural effects which occur in the chosen mixtures as for evaluating the efficiency and the predictive capability of the solution models[1]. Density and viscosity are important basic data used in process simulation, equipment design, solution theory and molecular designs. Ternary mixtures with alcohols as one component are indispensable for the industrial rectification column to avoid the formation of azeotropes[2] .

A third component added to a mixture of two immiscible components brings about the disappearance of the phase boundary resulting in a homogeneous mixture. This phenomenon in certain ternary liquid mixtures has been studied earlier[3-6] by observations on the distribution of molecules of one component between the other two components and by looking for the formation of hitherto unknown compounds from a study of the change in adiabatic compressibility, free volume and internal pressure.

2. Theoretical Considerations

Assuming that absorption of acoustic wave is negligible, the adiabatic compressibility (β_{ad}) can be calculated from Laplace's equation:

$$\beta_{ad} = 1/\rho U^2 \qquad\qquad 1$$

in which u is the ultrasonic velocity and ρ is the density.

Intermolecular free length (L_f) has been evaluated from Jacobson's formula[7,8]

$$L_f = K \beta_{ad}^{1/2} \qquad\qquad 2$$

where K is Jacobson's constant which is a temperature dependent constant but independent of the nature of the liquid. The value of K= 4.28 X 10^9

Thermodynamic excess functions were found be very sensitive towards mutual interactions between component molecules of liquid mixtures. The sign and extent of deviation of these functions from ideality depends on the strength of interaction between unlike molecules[9].

The excess functions (Y^E) were calculated by using the relations.

$$Y^E_{cal} = Y_{exp} - Y_{ideal} \qquad\qquad 3$$

$$Y^E_{cal} = Y_{exp} - [X_1Y_1 + X_2Y_2 + X_3Y_3] \qquad\qquad 4$$

where Y stands for V^E, $\Delta\beta$, L_f^E, $\Delta\eta$, X is the mole fraction. Subscripts 1,2 &3 refer to pure components respectively.

International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064, Impact Factor (2013): 4.438
www.ijsr.net

Table 1: Ultrasonic velocities, Densities, Viscosities and related Acoustic Parameters at 303.15K

Mole fraction			U	$\rho \times 10^{-3}$	η	V	$\beta_{ad} \times 10^{-12}$	$L_f \times 10^{-10}$
x_1	x_2	x_3	ms^{-1}	$kg\ m^{-3}$	cp	$Cm^3 mol^{-1}$	$m^2 N^{-1}$	m
Ethyl benzoate +Benzene +NN-dimethyl formamide								
0.2132	0.0000	0.7868	1415.87	0.9915	1.3580	90.2888	50.3108	0.4447
0.2154	0.0689	0.7157	1409.25	0.9894	1.3367	91.0075	50.8923	0.4473
0.2178	0.1392	0.6430	1399.42	0.9864	1.3078	91.8270	51.7682	0.4511
0.2201	0.2111	0.5688	1387.99	0.9819	1.2804	92.7988	52.8635	0.4559
0.2226	0.2846	0.4929	1374.62	0.9760	1.2428	93.9306	54.2232	0.4617
0.2250	0.3597	0.4153	1360.42	0.9697	1.1986	95.1273	55.7207	0.4680
0.2276	0.4364	0.3360	1347.48	0.9618	1.1489	96.5133	57.2625	0.4745
0.2302	0.5150	0.2549	1334.54	0.9537	1.1019	97.9566	58.8742	0.4811
0.2328	0.5953	0.1719	1321.47	0.9451	1.0456	99.4918	60.5909	0.4881
0.2355	0.6775	0.0869	1309.27	0.9360	0.9844	101.1243	62.3255	0.4950
0.2383	0.7617	0.0000	1295.76	0.9276	0.9108	102.7271	64.2081	0.5024
Ethyl benzoate +Benzene +NN-dimethyl acetamide								
0.2455	0.0000	0.7545	1420.01	0.9641	1.4134	106.4223	51.4393	0.4497
0.2448	0.0782	0.6770	1399.23	0.9612	1.3169	105.9641	53.1396	0.4571
0.2441	0.1560	0.5999	1380.70	0.9583	1.2370	105.4984	54.7365	0.4639
0.2433	0.2333	0.5233	1364.00	0.9554	1.1680	105.0516	56.2607	0.4703
0.2426	0.3102	0.4472	1349.27	0.9523	1.1109	104.6187	57.6826	0.4762
0.2419	0.3866	0.3716	1336.00	0.9487	1.0612	104.2337	59.0526	0.4818
0.2411	0.4625	0.2964	1324.71	0.9446	1.0202	103.9186	60.3260	0.4870
0.2404	0.5379	0.2216	1315.03	0.9403	0.9864	103.6239	61.4979	0.4917
0.2397	0.6130	0.1473	1306.22	0.9355	0.9556	103.3857	62.6505	0.4963
0.2390	0.6876	0.0734	1298.13	0.9304	0.9306	103.1853	63.7830	0.5007
0.2383	0.7617	0.0000	1291.26	0.9244	0.9108	103.0834	64.8807	0.5050
Methyl benzoate +Benzene +NN-dimethyl formamide								
0.2357	0.0000	0.7643	1426.20	0.9880	0.9274	89.021	49.7602	0.4423
0.2381	0.0669	0.6950	1410.97	0.9860	0.9264	89.703	50.9458	0.4475
0.2406	0.1351	0.6242	1398.17	0.9838	0.9314	90.406	51.9951	0.4521
0.2432	0.2049	0.5520	1385.4	0.9825	0.9424	91.048	53.0298	0.4566
0.2458	0.2761	0.4782	1373.3	0.9809	0.9520	91.731	54.0579	0.4610
0.2484	0.3488	0.4028	1361.3	0.9784	0.9620	92.506	55.1528	0.4656
0.2511	0.4231	0.3257	1348.0	0.9731	0.9677	93.572	56.5544	0.4715
0.2539	0.4991	0.2470	1333.9	0.9667	0.9511	94.771	58.1408	0.4781
0.2567	0.5768	0.1665	1317.9	0.9583	0.9171	96.193	60.0816	0.4860
0.2596	0.6562	0.0842	1301.8	0.9493	0.8659	97.712	62.1565	0.4943
0.2626	0.7374	0.0000	1286.00	0.9404	0.8048	99.272	64.2971	0.5028
Methyl benzoate +Benzene +NN-dimethyl acetamide								
0.2703	0.0000	0.7297	1424.30	0.9712	1.0025	103.350	50.7561	0.4467
0.2695	0.0757	0.6548	1413.81	0.9668	0.9680	103.075	51.7467	0.4510
0.2687	0.1509	0.5803	1404.31	0.9620	0.9369	102.846	52.7109	0.4552
0.2679	0.2257	0.5063	1396.48	0.9571	0.9078	102.630	53.5772	0.4589
0.2672	0.3001	0.4327	1386.91	0.9521	0.8831	102.428	54.6056	0.4633
0.2664	0.3740	0.3596	1374.63	0.9471	0.8646	102.222	55.8762	0.4687
0.2656	0.4476	0.2868	1360.30	0.9420	0.8497	102.033	57.3690	0.4749
0.2649	0.5206	0.2145	1345.59	0.9362	0.8362	101.923	58.9942	0.4816
0.2641	0.5933	0.1426	1329.71	0.9305	0.8245	101.804	60.7817	0.4888
0.2633	0.6656	0.0711	1311.59	0.9243	0.8130	101.743	62.8917	0.4972
0.2626	0.7374	0.0000	1286.00	0.9180	0.8048	101.697	65.8681	0.5089

International Symposium on Ultrasonics-2015, 22-24 January 2015
Department of Physics, Rashtrasant Tukdoji Maharaj Nagpur University, Nagpur, Maharashtra, India

44

International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064, Impact Factor (2013): 4.438
www.ijsr.net

Table 2: Excess molar volume(V^E), deviation in adiabatic compressibility ($\Delta\beta_{ad}$), excess intermolecular free length (L_f^E) and deviations in viscosity ($\Delta\eta$) at 303.15K

Mole fraction			V^E cm^{3}mol^{-1}	$\Delta\beta_{ad}\times10^{-12}$ m^{2}N^{-1}	$L_f^E\times10^{-10}$ m	$\Delta\eta$ cp
x_1	x_2	x_3				
Ethyl benzoate + Benzene + NN-dimethyl formamide						
0.2132	0.0000	0.7868	-1.5594	-1.4097	-0.0061	0.3583
0.2154	0.0689	0.7157	-1.8196	-2.1191	-0.0088	0.3674
0.2178	0.1392	0.6430	-2.0000	-2.5620	-0.0103	0.3891
0.2201	0.2111	0.5688	-2.0500	-2.8141	-0.0110	0.4125
0.2226	0.2846	0.4929	-1.9624	-2.8317	-0.0107	0.3860
0.2250	0.3597	0.4153	-1.8332	-2.7419	-0.0101	0.2531
0.2276	0.4364	0.3360	-1.5387	-2.6396	-0.0094	0.2149
0.2302	0.5150	0.2549	-1.2118	-2.5002	-0.0088	0.1797
0.2328	0.5953	0.1719	-0.8187	-2.2897	-0.0079	0.1355
0.2355	0.6775	0.0869	-0.3549	-2.0964	-0.0072	0.0867
0.2383	0.7617	0.0000	-0.0517	-1.7914	-0.0059	0.0258
Ethyl benzoate + Benzene + NN-dimethyl acetamide						
0.2455	0.0000	0.7545	-0.6255	-6.0000	-0.0029	0.2834
0.2448	0.0782	0.6770	-1.6600	-6.5600	-0.0560	0.2121
0.2441	0.1560	0.5999	-2.3410	-7.2000	-0.0575	0.1572
0.2433	0.2333	0.5233	-2.9700	-7.6772	-0.0606	0.1130
0.2426	0.3102	0.4472	-3.4000	-8.2490	-0.0625	0.0806
0.2419	0.3866	0.3716	-3.6500	-8.5855	-0.0625	0.0555
0.2411	0.4625	0.2964	-3.1900	-8.7197	-0.0631	0.0389
0.2404	0.5379	0.2216	-2.5000	-8.4104	-0.0619	0.0294
0.2397	0.6130	0.1473	-1.7700	-7.2500	-0.0606	0.0227
0.2390	0.6876	0.0734	-0.9700	-5.3100	-0.0575	0.0218
0.2383	0.7617	0.0000	-0.4080	-4.5000	-0.0500	0.0258
Methyl benzoate + Benzene + NN-dimethyl formamide						
0.2357	0.0000	0.7643	-0.1987	-0.8383	-0.0036	0.0424
0.2381	0.0669	0.6950	-0.4400	-0.8947	-0.0034	0.1800
0.2406	0.1351	0.6242	-0.6800	-1.1134	-0.0039	0.3030
0.2432	0.2049	0.5520	-1.0000	-1.3734	-0.0047	0.4590
0.2458	0.2761	0.4782	-1.3000	-1.6678	-0.0056	0.4840
0.2484	0.3488	0.4028	-1.5300	-1.9239	-0.0064	0.4640
0.2511	0.4231	0.3257	-1.4900	-1.9028	-0.0061	0.4260
0.2539	0.4991	0.2470	-1.3400	-1.7273	-0.0052	0.3360
0.2567	0.5768	0.1665	-0.9900	-1.2289	-0.0031	0.3180
0.2596	0.6562	0.0842	-0.5680	-0.6290	-0.0007	0.1310
0.2626	0.7374	0.0000	-0.1300	-0.0029	-0.0016	0.0505
Methyl benzoate + Benzene + NN-dimethyl acetamide						
0.2703	0.0000	0.7297	-1.0255	-0.1684	-0.0006	0.0889
0.2695	0.0757	0.6548	-1.0511	-0.5500	-0.0018	0.0992
0.2687	0.1509	0.5803	-1.1200	-0.9500	-0.0031	0.1062
0.2679	0.2257	0.5063	-1.2000	-1.4400	-0.0049	0.1114
0.2672	0.3001	0.4327	-1.2930	-1.7600	-0.0059	0.1123
0.2664	0.3740	0.3596	-1.3800	-1.8300	-0.0059	0.1071
0.2656	0.4476	0.2868	-1.4830	-1.6700	-0.0051	0.0985
0.2649	0.5206	0.2145	-1.6621	-1.3700	-0.0037	0.0886
0.2641	0.5933	0.1426	-1.5315	-0.9000	-0.0018	0.0770
0.2633	0.6656	0.0711	-0.0571	-0.1000	-0.0013	0.0654
0.2626	0.7374	0.0000	-0.2956	-0.0740	-0.0007	0.0506

3. Results and Discussion

In the present study, the ultrasonic velocity, density and viscosity have been measured at the temperature of 303.15K for the following systems:

System – I Ethyl benzoate(A) +benzene(B) + N-N-dimethyl formamide(C)

System – II Ethyl benzoate(A) +benzene (B)+ N-N-dimethyl acetamide(C)

System – III Methyl benzoate (A)+benzene(B) + N-N-dimethyl formamide(C)

System – IV Methyl benzoate(A)+benzene(B) + N-N-dimethyl acetamide(C)

45

International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064, Impact Factor (2013): 4.438
www.ijsr.net

The experimental results of ultrasonic velocity, density and viscosity along with computed values of molar volume(V), adiabatic compressibility(β_{ad}) and intermolecular free length(L_f) for the four ternary liquid mixtures at 303.15K are given in Table 1.The values of excess thermodynamic functions viz. the excess molar volume(V^E) , excess intermolecular free length(L_f^E) along with deviation in adiabatic compressibility($\Delta\beta_{ad}$) and deviation in viscosity($\Delta\eta$) are presented in Table 2.The non- linear variation of these parameters with the change of composition of the ternary mixtures indicates presence of molecular interaction between the mixing components[10-13].

A close perusal of the above mentioned tables reveal that ultrasonic velocity shows decreasing trend with mole fraction of benzene for all the four ternary systems. The addition of benzene into the binary system of Ethyl benzoate + NNDMF or Ethyl benzoate + NNDMAc disturbs the existing dipole-dipole interactions between component molecules and leads to a weaker interaction of the dipole-induced dipole type both with ethyl benzoate and NNDMF/NNDMAc and hence the ultrasonic velocity decreases with increase in benzene concentration. Similar trends were observed when ethyl benzoate (component A) is replaced by methyl benzoate. Further it is observed that interaction becomes stronger in ternary mixtures involving ethyl benzoate.

The strong dipolar association of AC interaction is disrupted by the addition of benzene (B) in all the four systems. This leads to a very weak AB & BC interaction of dipole – induced dipole type which leads to reduction in total interaction of the system. As the concentration of component B increases the net interaction of the system keeps on decreasing for any particular system. This is very well reflected by the observed trend in ultrasonic velocity. The weak dipole-induced dipole type of interaction is evident by the linear variation of ultrasonic velocity with the concentration of component B.

A close perusal of compressibility values of system-I and system-II indicates that compressibility values of liquid mixtures are close to compressibility of component of A (ethyl benzoate). It is observed that β and L_f show an exact reverse trend as that of ultrasonic velocity. It is primarily the compressibility that changes with the structure and this lead to change in ultrasonic velocity[14].The addition of interacting molecules breaks up the molecular clustering of the other releasing several dipoles for interactions. In view of greater force of interaction between the molecules there will be an increase in cohesive energy and the occurrence of structural changes, takes place due to existence of electrostatic field. Thus structural arrangement of molecules results in increasing adiabatic compressibility there by showing progressively intermolecular interactions. Similar results in some liquid mixtures were also reported by Bhatti and Singh[15].

The increase in concentration of benzene weakens the net interaction in the systems and makes the molecules to move apart. This makes the system more compressible. Benzene being a bulky molecule may enhance the void in the system at the extent of reduction in component C (NNDMF/NNDMAc) which is aliphatic. This reduces the compactness of the system and may also be a reason for the more compressible nature of the systems.

Intermolecular free length is found to be a predominating factor which depends upon the adiabatic compressibility and shows similar behavior as that of compressibility. On the basis of sound propagation in liquid, the increase in free length results a decrease in the velocity.[16,17]

The variation of L_f, shows similar trend as that of β_{ad} which confirms the existing interaction. The viscosity values of the system show a decreasing trend with concentration of component B (benzene). The reduction in viscosity may arise due to reduction in effective molecular area or weak interaction between component molecules.

The reduction in the viscous nature in all the systems is also observed by the decrease in behavior of internal pressure. Internal pressure is the resultant of the forces of attraction and repulsion between the component molecules in the solution. As concentration of component B (benzene) increases, the repulsive forces of π – electron clouds of aromatic rings of component A(ethyl benzoate/methyl benzoate) & B(benzene) become predominant and also the disruption of dipolar association of AC and very weak AB, BC interactions may be the reason for the observed trend of internal pressure in all the four systems.

The free volume shows reverse trend as to internal pressure. The increase in free volume may be due to weakening of interaction and also due to the replacement of component C(NNDMF/NNDMAc) by bulky component B(benzene) molecules.

In order to understand more about the nature of interaction between components of liquid mixtures, it is necessary to discuss the same in terms of excess parameters rather than actual values. They can yield an idea about the non linearity of the system and as association or other type of interactions[18].

It is a well established fact that signs and magnitude of V^E provides a good estimate of strength of unlike interactions in a ternary mixture. Positive values of excess volume indicate weak intermolecular interactions, whereas negative values of V^E usually point towards strong interactions and formation of intermolecular complexes[19]. Exhaustive studies of V^E of multi component systems reveal that strength of interaction between two components is weakened by the addition of third component. Thus, a ternary system seems to be a fairly good example of the extent of weakening of interactions proportional to the number of components. It has also been observed that the V^E of mixing of liquids can arise from any one of the following factors:
1) Difference in intermolecular interaction energy between like and unlike molecules.
2) Difference in size and shape of component molecules.
3) Structural changes such as changes in the correlation of molecular orientation and
4) Formation of new chemical species through hydrogen bonding or electron donor-acceptor interactions.

The excess value is the result of two opposing effects: self dissociation and physical dipole–dipole interactions between ring structured component liquids, which lead to volume increase and negative contributions arising from change of free volume in the liquid mixture resulting from collapse of order in the mixture. This increased disorder of the breaking of ordered structure predominates the loss in free volume resulting in negative values of excess volume. The sign further reflects superposition of size effect upon another which causes contraction that may arise from disruption by mixing process of somewhat expanded dipole-dipole structure.

It can be seen from Table 5.2 that the deviation in adiabatic compressibility is negative over entire range of molefraction for all the systems. Sridevi et al[20] suggested that the negative excess compressibility is due to closely packed molecules and positive excess values are due to weak interaction between the unlike molecules. Similar conclusions were also arrived by Islam and Quadri[21].

The values of excess intermolecular free length follow the same trend as that of $\Delta\beta_{ad}$. The excess free length values are negative and show increasing trend in all the four systems under study. It is reported that interaction between aliphatic and aromatic molecules is very stronger[22].

According to Vogel and Weiss[23], mixtures with strong interactions between different molecules result in positive viscosity deviations, whereas, for mixtures without strong interactions the viscosity deviations are negative. The positive values of $\Delta\eta$ in all the four ternary systems is supported by the negative values of V^E.

4. Conclusions

1) The strong dipolar association of AC interaction is disrupted by the addition of benzene (B). This leads to a very weak AB & BC interaction of dipole – induced dipole type which leads to reduction in total interaction of the system.
2) Thus structural arrangement of molecules results in increasing adiabatic compressibility there by showing progressively intermolecular interactions.
3) The variation of L_f, shows similar trend as that of β_{ad} which confirms the existing interaction.
4) The deviation in adiabatic compressibility is negative over entire range of molefraction for the four systems.
5) The positive values of $\Delta\eta$ in all the four ternary systems is supported by the negative values of V^E.

References

[1] Trenzado J L, Matos J S, Gonzalez E, Romano E & Caro M N, J Chem Eng Data, 48 (2003) 1004.
[2] Devadoss D, Thairiyaraja M & Palaniappan, Indian J. Phys, 77B(6) (2003) 669.
[3] Kannapan V, Jaya Santhi R & Malar E J P, Phys Chem Liq, 40 (2002) 507.
[4] Kwaterski M, Rezanova E N & Lichtenthaler R N, J Chem Thermodyn, 38 (2006) 1199.
[5] Geetha D & Rakkapan C, Indian J Phys, 77B (5) (2003) 525.
[6] Prasad N, Indian J Pure Appl Ultrason, 25 (2003) 25.
[7] Jacobson B, Acta Chem Scand, 6 (1952) 485
[8] Jacobson B, J Chem Phys, 20 (1952) 927.
[9] Aminabhavi T M, Manjeshwar L S, Halligudi S B & Balundgi R H, Indian J Chem, 28A (1989) 217.
[10] Rout B K, Chakravortty V & Behera D, Indian J Tech, 31(1993) 745.
[11] Rout B K, Mishra N C & Chakravortty V, Indian J Chem Tech, 1(1994)347.
[12] Rout B K, & Chakravortty V, Indian J Chem, 33A (1994) 303.
[13] Rout B K, Chakravortty V & Samal K, Acoust Letters, 17(1994) 203.
[14] Nikam P S, Kapade V M, & Mehdi Hasan, Indian J Pure Appl Phys, 38(2000)170.
[15] Bhatti S S, & Singh D P, Indian J Pure Appl Phys, 21 (1983) 506.
[16] Madhu Rastogi, Aashees Awasthi, Manisha Gupta & Shukla J P, Indian J Pure Appl Phys, 40 (2002) 256.
[17] Arul G, Palaniappan L, Indian J Pure Appl Phys, 39 (2001)561.
[18] Kannapan A N, Kesavasamy R, Ponnuswamy V, ARPN J Engg Appl Sci,3(2008)41.
[19] Ranjan Dey, Anjan Chattopadhyay, Ashish K Sharma & Pandey J D, J Mol Liq, 147(2009) 155.
[20] Sridevi U, Samatha K, Viswanatha Sarma A, J Pure Appl Ultrason,26(2004)1.
[21] Islam M R & Quadri, Thermo Chim Acta, 115(1987)335.
[22] Kumar R, Ph.D Thesis, University of Madras, September(2009).
[23] Vogel H, Weiss A, Ber Bensen-Ges,86(1982)193.

International Symposium on Ultrasonics-2015, 22-24 January 2015
Department of Physics, Rashtrasant Tukdoji Maharaj Nagpur University, Nagpur, Maharashtra, India
Licensed Under Creative Commons Attribution CC BY

47