ULTRASONIC STUDY IN TERNARY LIQUID MIXTIRE OF BENZENE + TRIMETYHYL AMINE +ACETIC ACID AND BENZENE + TRIETYHYL AMINE +ACETIC ACID AT DIFFERENT TEMPERATURES

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ABSTRACT

The ultrasonic velocity, viscosity and density of ternary liquid mixtures of different compositions have been made at different temperatures in the ternary liquid mixtures of benzene + tri-methylamine +acetic acid and benzene + tri-ethylamine +acetic acid at different temperature. Various thermodynamic and acoustical parameters were calculated. The results were explained in terms of dipole-dipole interactions and hydrogen bon formation between acetic acid and tri-ethylamine.

Key Words: *Carboxylic acids, tri-methyl amine, molecular interactions, Ternary liquid mixtures, Ultrasonic study*

Introduction

The molecules in a liquid are so close together that the various interactions such as Vander Waal's forces, electronic fields and ionic interactions assume considerable significance. Since these factors are not easy to evaluate, it is expedient to heavily rely on experimental information in characterizing liquids. The data may be classified according to the equilibrium and non-equilibrium conditions of the fluid. The consideration of collection of thermodynamic properties makes up the first category, while the second involves the transport phenomenon.

Of the several physical properties of liquids which can be employed to study the various molecular interactions prevailing therein, we have chosen

i. Density
ii. Viscosity and
iii. Ultrasonic velocity.

Viscosity

A factor, bulk flow, is introduced by transport process of viscous flow. Momentum is transferred and this transfer will have significance only if one layer of fluid moves relative to other. Even though momentum is randomly exchanged the net movement will be in the forward direction for the bulk of fluid.

For a flow of fluid in the cylindrical tube the portion of the fluid along the axis moves with a greater velocity than that closer to the wall, with resultant velocity gradient from the centre outward. The force causing the flow in the x-direction of one segment of fluid past another one parallel to it produces the gradient, $\frac{dv}{dy} and f = -\eta\frac{dv}{dy}$ Where η *is* coefficient of viscosity. Here the gradient is along y direction.

Viscosity is measured by noting the time taken by *a* given volume of liquid to flow through a capillary tube. Departure of viscosity of liquid mixtures from that of ideal ones can be studied by viscosity measurements.

Ultrasonic Velocity

Vibrational waves of frequency above hearing range of the normal ear are referred to as ultrasonic waves. All waves above 20 KHz are ultrasonic waves. The upper limit of ultrasonic does not depend upon any intrinsic physical property of ultrasonics, but on the technical difficulty of producing such waves. However the upper frequency limit is of the order of 100 MHz.

Systems Undertaken

System I: Benzene +Tri-ethyl amine (TEA) + Acetic Acid
System II: Benzene +Tri-methyl amine (TMA) + Acetic Acid
Temperatures: 303K, 308 K, 313 K

Sample Preparation and Measurement

The liquids used were of BDH AR grade and were redistilled before use. Samples of different concentrations were prepared by mixing the component liquids in volume proportion. Every time 28 ml was prepared for measurement of density, viscosity and ultrasonic velocity.

For density measurement the density bottle was filled with the sample mixture and then immersed up to the neck in thermostatic bath for five minutes. After that it was wiped out from outside, cooled up to room temperature and weighed using monopan balance.

For viscosity measurements Ostwald viscometer was filled with given liquid and was immersed into constant temperature water bath for about 5 minutes to acquire the desired constant temperature. The time‘t’ for liquid to go from mark A to lower mark B was recorded, with astop watch of accuracy.

Materials and Methods

In the present investigation density, viscosity and ultrasonic velocity are measured for ternary liquid mixtures containing Benzene + Tri-methyl amine + Acetic acid and Benzene + Tri-ethyl amine + Acetic and acid at three different temperatures 303K, 308Kand 313K. The chemicals were of AR grade obtained from Merc, Mumbai with purity of 99.5% .The mixtures were prepared at room temperature by mixing the components in volume proportion.

The density measurements were made by using electronic monopan balance supplied byCONTECH with accuracy of 0.0001 gm and specific gravity bottle of 10ml capacity.

Viscosity was made by using Ostwald’s viscometer. The time of flow was measured with digital stop watch.

The sound velocity was measured by using ultrasonic multiple frequency interferometer supplied by Mittal enterprises New Delhi working at 3 MHz (Model No. M815)

In order to maintain the temperature of the mixture constant the temperature controlled water bath was used. The density bottle and viscometer were immersed in bath for 10 minutes to attain the desired temperature. In order to keep the temperature of the mixture constant the constant temperature water bath supplied by BIOTECNICS INDIA with accuracy of 0.5 ^{o}C was used. The hot water of the bath was circulated through the metal Jacket of the cell of the interferometer.

Result and Discussion

Tables for System-I (Benzene + Tri-ethyl amine + Acetic acid)

TABLE No.1: Temp.303K (35^{o}C)

Mole Fraction Of Tri-ethyl amine	Density ρ (gmcm^{-3}	Viscosity η (cp)	Velocity U (m/s)	Molar volume V (cm^{3}/mole)	Adiabatic compressibility βa (cm^{2}/dyne)	Freelength Lf (A^{o})	Available Volume Va (cm^{3}/mole)	Specific acoustical impedence Z (dyne s cm^{-3})
0.3902	0.8428	0.4745	1171.5	103.367	8.65E-11	0.5867	27.68	987.33
0.3097	0.8801	0.7129	1197.0	94.300	7.93E-11	0.5619	23.75	1053.44
0.2403	0.9263	1.1614	1232.4	85.752	7.11E-11	0.5320	19.70	1141.60
0.1799	0.9769	1.9015	1305.6	78.137	6.00E-11	0.4890	14.38	1275.49
0.1267	1.0029	2.0839	1321.8	73.399	5.71E-11	0.4767	12.76	1325.61
0.0797	1.0010	1.5639	1271.4	71.125	6.18E-11	0.4960	14.61	1272.70
0.0377	1.0042	1.4719	1204.5	68.760	6.86E-11	0.5228	17.00	1209.51
0.0000	1.0004	0.6560	1147.5	67.089	7.59E-11	0.5498	18.97	1147.93

TABLE No.2 : Temp.308K (35°C)

Mole Fraction Of Triethylamine	Density ρ ($gmcm^{-3}$)	Viscosity η (cp)	Velocity U (m/s)	Molar volume V (cm^3/mole)	Adiabatic compressibility βa (cm^2/dyne)	Freelength Lf (A^o)	Available Volume Va (cm^3/mole)	Specific acoustical impedence Z (dyne s cm^{-3})
0.3894	0.8381	0.4446	1135.2	80.5765	9.26E-11	0.6120	23.4075	951.41
0.2219	0.8854	0.6778	1173.0	67.2603	8.21E-11	0.5762	17.9501	1038.61
0.1756	0.9242	1.0542	1215.9	62.9035	7.32E-11	0.5441	15.1008	1123.71
0.1338	0.9764	1.5267	1275.9	58.2256	6.29E-11	0.5045	11.7943	1245.75
0.0958	0.9959	1.6982	1310.1	55.9132	5.85E-11	0.4865	10.1308	1304.69
0.0611	0.9983	1.3546	1250.7	54.7083	6.40E-11	0.5089	11.9435	1248.60
0.0293	0.9972	1.1929	1185.0	53.7926	7.14E-11	0.5375	13.9525	1181.63
0.0000	0.9926	0.6213	1128.9	53.1332	7.91E-11	0.5655	15.6444	1120.57

TABLE No.3 : Temp.313K (35°C)

Mole Fraction Of Triethylamine	Density ρ ($gmcm^{-3}$)	Viscosity η (cp)	Velocity U (m/s)	Molar volume V (cm^3/mole)	Adiabatic compressibility βa (cm^2/dyne)	Freelength Lf (A^o)	Available Volume Va (cm^3/mole)	Specific acoustical impedance Z (dyne s cm^{-3})
0.3901	0.8286	0.4057	1131.6	105.1368	9.43E-11	0.6233	30.7788	937.61
0.3094	0.8830	0.5910	1157.7	93.9696	8.45E-11	0.5902	25.9767	1022.23
0.2400	0.9212	0.9399	1194.9	86.2018	7.60E-11	0.5598	21.8252	1100.73
0.1795	0.9718	1.4212	1263.3	78.5194	6.45E-11	0.5155	16.5234	1227.68
0.1264	0.9919	1.5001	1291.2	74.1792	6.05E-11	0.4992	14.3166	1280.79
0.0794	0.9968	1.5565	1236.3	71.3966	6.56E-11	0.5201	16.2293	1232.37
0.0376	0.9919	0.9895	1161.6	69.5864	7.47E-11	0.5549	19.0667	1152.15
0	0.9907	0.5633	1109.1	67.7214	8.21E-11	0.5816	20.7778	1098.80

Tables for System- II (Benzene + Tri-methyl amine + Acetic acid)

TABLE No.4 : Temp.303K (35°C)

Mole Fraction Of Tri-methyl amine	Density ρ ($gmcm^{-3}$)	Viscosity η (cp)	Velocity U (m/s)	Molar volume V (cm^3/mole)	Adiabatic compressibility βa (cm^2/dyne)	Free length Lf (A^o)	Available Volume Va (cm^3/mole)	Specific acoustical impedance Z (dyne s cm^{-3})
0.5807	0.9544	1.6214	1219.2	70.2781	7.05E-11	0.5298	16.7262	1163.66
0.4927	1.0051	2.7295	1380.0	66.7438	5.22E-11	0.4561	9.1773	1387.01
0.4064	1.0195	3.4360	1270.8	65.8049	6.07E-11	0.4918	13.5393	1295.58
0.3219	1.0826	3.2979	1262.1	61.9751	5.80E-11	0.4805	13.0884	1366.34
0.2391	1.0310	2.9334	1253.4	65.0844	6.17E-11	0.4958	14.0989	1292.20
0.1578	1.0515	2.7201	1221.3	63.8170	6.38E-11	0.5038	15.1047	1284.22
0.0781	1.0313	1.2552	1195.8	65.0704	6.78E-11	0.5196	16.4384	1233.28
0.0000	1.0004	0.6560	1147.5	67.0895	7.59E-11	0.5498	18.9738	1147.93

TABLE No.5 : Temp.308K (35°C)

Mole Fraction Of Tri-methyl amine	Density ρ ($gmcm^{-3}$)	Viscosity η (cp)	Velocity U (m/s)	Molar volume V (cm^3/mole)	Adiabatic compressibility βa (cm^2/dyne)	Free length Lf (A^o)	Available Volume Va (cm^3/mole)	Specific acoustical impedance Z (dyne s cm^{-3})
0.5813	0.9378	1.2870	1208.1	71.5098	7.31E-11	0.5436	17.5154	1133.00
0.4936	0.9852	1.8477	1222.2	68.0817	6.79E-11	0.5243	16.0758	1204.14
0.4075	1.0292	3.1115	1245.3	65.1839	6.27E-11	0.5034	14.4505	1281.65
0.3229	1.0691	2.8015	1244.4	62.7622	6.04E-11	0.4943	13.9489	1330.35
0.2400	1.0252	2.6043	1233.0	65.4582	6.42E-11	0.5094	15.0145	1264.07
0.1585	1.0499	2.5342	1198.5	63.9289	6.63E-11	0.5179	16.0422	1258.29
0.0786	1.0265	1.1984	1176.9	65.3965	7.03E-11	0.5334	17.2933	1208.06
0.0000	0.9926	0.6213	1128.9	67.6367	7.91E-11	0.5655	19.9148	1120.57

TABLE No.6 : Temp.313K (35°C)

Mole Fraction Of Tri-methyl amine	Density ρ ($gmcm^{-3}$)	Viscosity η (cp)	Velocity U (m/s)	Molar volume V (cm^3/mole)	Adiabatic compressibility βa (cm^2/dyne)	Freelength Lf (A°)	Available Volume Va (cm^3/mole)	Specific acoustical impedence Z (dyne s cm^{-3})
0.5812	0.9317	0.9598	1207.2	71.9862	7.37E-11	0.5510	17.6726	1124.706
0.4930	0.9848	1.6855	1265.1	68.1062	6.34E-11	0.5114	14.2555	1245.868
0.4066	1.0306	2.8532	1228.2	65.0862	6.43E-11	0.5149	15.1244	1265.723
0.3219	1.0674	2.5407	1218.9	62.8405	6.31E-11	0.5098	14.9678	1301.101
0.2390	1.0227	1.9211	1213.8	65.5928	6.64E-11	0.5230	15.8325	1241.358
0.1577	1.0496	2.1684	1182.3	63.9139	6.82E-11	0.5300	16.6855	1240.97
0.0781	0.9092	0.9725	1148.4	73.7896	8.34E-11	0.5863	20.8271	1044.118
0.0000	0.9907	0.5633	1109.1	67.7214	8.21E-11	0.5816	20.7778	1098.799

1) Density

The Densities of (**System I**) *Benzene + Tri-ethylamine + Acetic acid*& (**System II**) *Benzene + Tri-methylamine +Acetic acid* at temperatures 303, 308, 313 K is presented in Table-1 to Table -6. From these values graphs of density vs. mole fraction of tri-ethylamine for system I and graph of density Vs mole fraction of tri-methylamine for system II have been plotted in Fig.1(a) and Fig.2(a). From these graphs it is observed that the density increases with mole fraction, attains maximum and decreases again. The density of the mixture is indicative parameter of molecular interactions. This non-linear behavior of density shows certainly the presence of molecular interactions among the components of the mixture. And as the temperature increases the density decreases. The variation of density with concentration and temperature can be attributed to the structural changes in mixture.

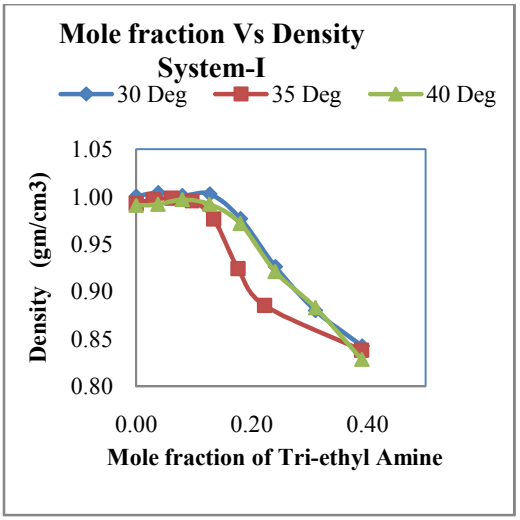

Fig. 1(a)

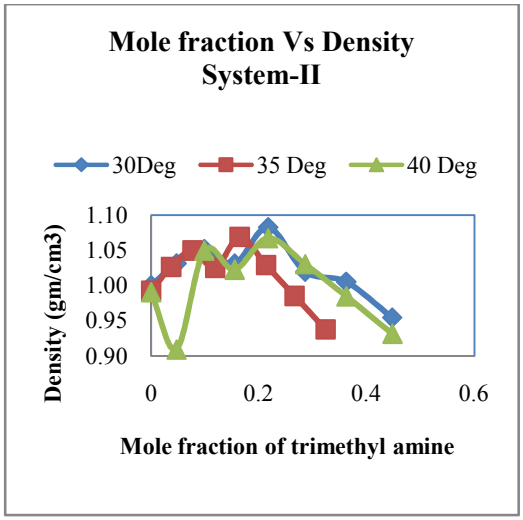

Fig. 2(a)

2) Viscosity

The values of viscosity for ternary liquid mixtures of different concentrations are measured at temperature 303K, 308K, 313K and are plotted in Fig.2 (a) and Fig.2 (b). For system I viscosity values increase with mole fraction of tri-ethylamine become maximum at certain mole fraction again it decrease. Similar behavior is observed in system II i.e. viscosity increases with mole fraction of tri-methylamine, becomes maximum and again decreases after certain value of mole fraction. The increasing trend of viscosity is the indication of frictional resistance and that may be due to change in effective molecular area of the cohesive or adhesive forces or relative random velocity between the components of

the mixture.The same findings were observed by number of authors[1, 2]. Such predictions of molecular interactions were made by J B Thakareet al[3] in Benzene+Caprylicacid+iso-butyl amine while interpreting results about excess free volume and excess compressibility. The viscosity of a liquid arises because of intermolecular forces. As the temperature increases viscosity decreases. The reason is that when the system temperature increases, it gives the molecules of the mixture the required energy in the form of thermal energy to overcome intermolecular forces. When this happens, the molecules move further apart and this decreases the viscosity of the fluid. The viscosity at maxima is of sufficiently higher order of magnitude in system II than system I. This suggests that the extent of complexation between molecules of tri-methylamine and acetic acid (system II) is greater than that between tri-ethylamine and acetic acid (system I). This may probably be due to greater value of viscosity of tri-methylamine than that of tri-ethylamine.

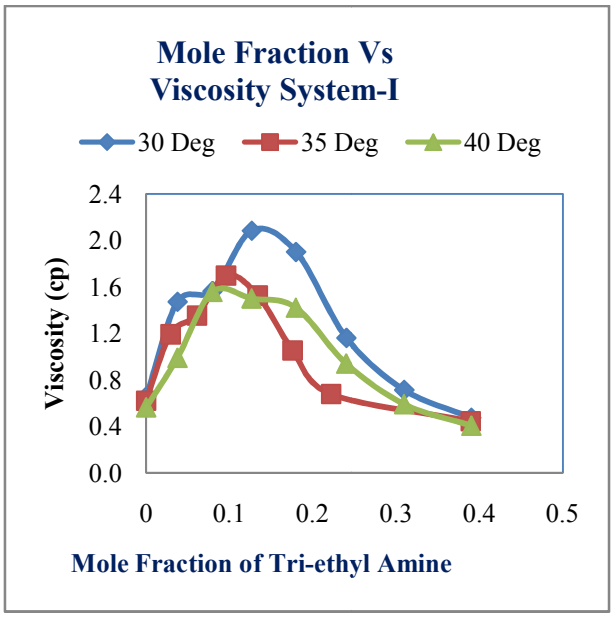

Fig.2 (a)

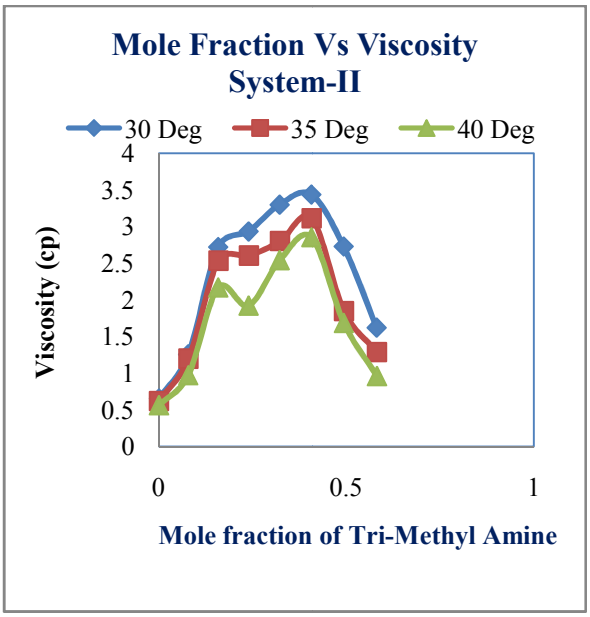

Fig.2 (b)

3) Velocity

The graphs in Fig. 3(a) and Fig. 3(b) show variation of ultrasonic velocity for the two system studied at three temperatures 303K, 308K & 313K. The nature of overall variation of velocity curve is convex upward in both systems. The ultrasonic velocity increases with mole fraction becomes maximum & decreases again. As density increases the number of particles in a given region is increased and this leads to quick transfer of sound energy. For this reason velocity increases, this result is in accordance with Arul G and L Palaniappan. The increase in ultrasonic velocity in any mixtures indicates the maximum association among the molecules of a mixture. In case of liquid mixtures the variation in ultrasonic velocity with concentration can be taken as the measure of molecular interaction between the components. As ultrasonic curves increases , attains maxima &thereafter decreases this leads to the conclusion of complex formation in the mixture. Such complex formation between the constituents of mixture has been reported by no of authors. It can be seen that ultrasonic curves fall with rise of temperature of the both systems. This is anticipated because rise of temperature is accompanied by molecular agitation disrupting the molecular alignment & affecting the complexed species.

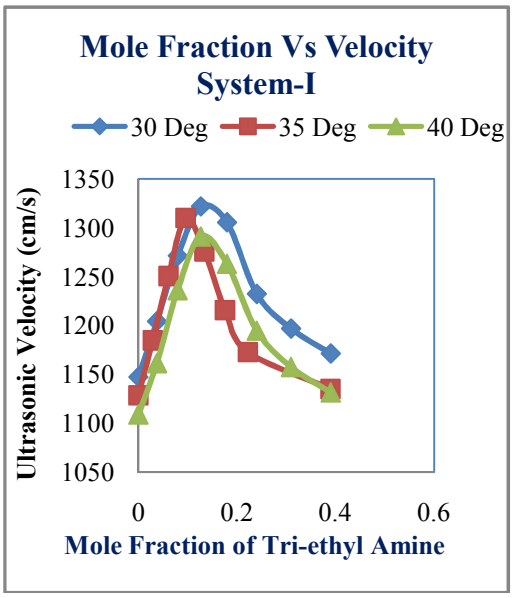

Fig.3 (a)

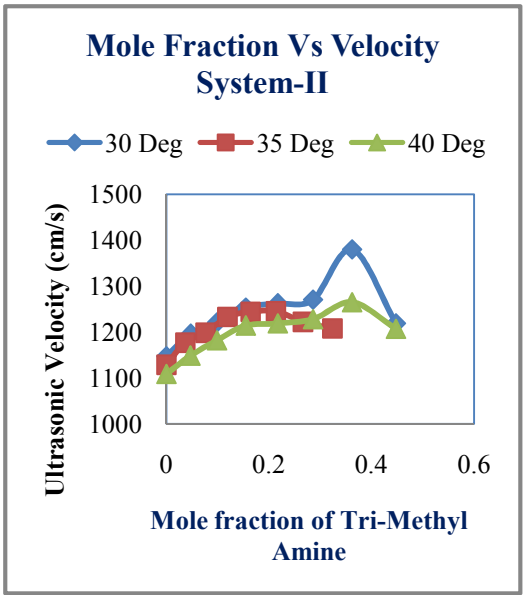

Fig.3 (b)

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