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ULTRASONIC STUDY OF TERNARY SOLUTIONS CONTAINING QUINOLINE

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Short Profile

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ABSTRACT:
The density (ρ) and velocity (U) of ultrasonic waves of 3 MHz frequency have been measured in ternary solutions of quinoline+methanol+benzene and quinoline+methanol+toluene at temperatures 303.15 K, 308.15 K, 313.15 K and 318.15 K over the entire composition range. From these experimental values several acoustical parameters have been calculated. The excess parameters are plotted against the mole fraction of quinoline over the whole composition range. The observed negative and positive values of excess parameters are explained in the light of intermolecular interactions present in these mixtures.

KEYWORDS
Benzene, toluene, quinoline, ultrasonic velocity, density

INTRODUCTION:

In continuation of our previous ultrasonic study of molecular interactions in quinoline with cresols1,2, the work has now been extended to the ternary solutions such as benzene and toluene in quinoline with methanol as mediator at temperatures 303.15, 308.15, 313.15 and 318.15K. Determination of the velocity of the propagated ultrasonic wave leads to the calculation of several very useful parameters, employed in ascertaining solutions, the degree of molecular association, dissociation, complex formation etc.

Density of liquid mixtures is required in most engineering calculations where fluid flow of mixture is an important factor. Moreover, knowledge of the dependence of densities of liquid mixtures on composition is of great interest from a theoretical stand point since it may lead to better understanding of the fundamental behaviour of liquid systems. Knowledge of density is essential in the design processes involving chemical separations, equipment design, solution theory heat transfer, fluid flow and molecular dynamics.

In chemical industry3,4 there exists a continuous need for reliable thermodynamic data of binary systems. Mixed solvents, rather than pure liquids find practical applications in many chemical and industrial processes. Their excess thermodynamic parameters enable us to understand the physico-chemical properties in a continuous manner.

The liquids used in the present study are important due to their various industrial applications. To increase the efficiencyquinoline is used in solar cells and also in dyes. Benzene is a natural constituent of crude oil, and is one of the most elementary petrochemicals. It is mainly used as a precursor to heavy chemicals, such as ethylbenzene and cumene, which are produced on a billion kilogram scale. It is an important component of gasoline. Toluene is a common solvent, able to dissolve paints, paint thinners, silicon sealants, many chemical reactants, rubber, printing ink, adhesives, lacquers, leather tanners and disinfectants. It is used as a solvent for carbon nanomaterials, including nanotubes and fullerenes.Toluene is also used as an octane booster in gasoline fuels used in internal combustion engines. It is recently used as component for jet fuel surrogate blends. Alcohols are self-associated organic liquids and are used as the basic organic compound for the synthesis of other organic compounds. The study of ternary mixtures of quinoline with benzene and toluene in methanol would be of considerable interest because these mixtures exhibit varying molecular interactions and are important from an industrial point of view.

EXPERIMENTAL

The analytical grade chemicals obtained from SRL Chemicals, Mumbai were used. They were purified by standard procedure5. To prepare the mixtures in the required proportions, Job's method of continuous variation was used. The mixtures were preserved in well-stoppard conical flasks. After mixing the liquids thoroughly, the flasks were left undisturbed to allow them to attain thermal equilibrium.

Single crystal ultrasonic pulse echo interferometer (Mittal enterprises, India; Model: F-80X) was used for measuring ultrasonic velocities. It consisted of a high frequency generator and a measuring cell. The measurements of ultrasonic velocities were made at a fixed frequency of 3MHz. The calibration of the equipment was done by measuring the velocity in benzene and carbon tetrachloride. The results are in good agreement with the literature values6. The ultrasonic velocity has an accuracy of ± 0.1 $m.s^{-1}$. The temperature is controlled by circulating water around the liquid cell from thermostatically controlled constant temperature water bath (accuracy ± 0.01K). Densities are measured by using specific gravity bottle.

THEORY

The values of Molar volume, V_m are calculated using standard relation,

$$V_m = M_{eff}/\rho \tag{1}$$

where $M_{eff} = (x_1M_1+x_2M_2+x_3M_3)$, M_1, M_2 and M_3 are the molecular weights of pure components, and ρ is the density of the mixture.
The acoustic impedance can be calculated by using the relation,

$$Z = \rho U \tag{2}$$

The strength of interaction between the component molecules of ternary mixtures is well reflected in the deviation of the excess functions from ideality7. The excess properties such as V_m^E, U^E, and Z^E are calculated by using the following equations

$$V_m^E = \left(\frac{x_1M_1 + x_2M_2 + x_3M_3}{\rho}\right) - \left(\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2} + \frac{x_3M_3}{\rho_3}\right) \tag{3}$$

$$U^E = U_m - [x_1U_1+x_2U_2+x_3U_3] \tag{4}$$

$$Z^E = Z_m - [x_1Z_1+x_2Z_2+x_3Z_3] \tag{5}$$

In equations (3), (4) and (5)ρ, U_m, Z_m and V_m are the density, ultrasonic velocity, acoustic impedance and molar volume of the mixture.

RESULTS AND DISCUSSION

System 1: quinoline + methanol + benzene
System 2: quinoline + methanol + toluene

The experimental values of ultrasonic velocity (U) and density (ρ) for the two systems at temperatures T = (303.15, 308.15, 313.15 and 318.15) K are given as a function of mole fraction in Table 1.

Table 1. Ultrasonic velocities (U) and densities (ρ) for the two systems at T = (303.15, 308.15, 313.15, and 318.15) K

x_1	x_3	U (m s^{-1})	r (Kg m^{-3})	x_1	x_3	U (m s^{-1})	r (Kg m^{-3})
System -1				System -2			
T = 303.15 K							
0.0000	0.8017	1269.00	859.85	0.0000	0.7720	1193.68	825.63
0.0694	0.7281	1283.57	883.20	0.0787	0.6916	1225.15	850.41
0.1418	0.6511	1305.73	903.35	0.1586	0.6099	1253.68	882.40
0.2175	0.5707	1326.05	925.60	0.2397	0.5269	1288.10	913.62
0.2967	0.4866	1350.89	950.98	0.3222	0.4426	1319.73	943.60
0.3797	0.3985	1370.78	974.11	0.4060	0.3569	1353.15	970.86
0.4667	0.3061	1397.36	998.77	0.4911	0.2699	1395.94	995.16
0.5580	0.2092	1430.47	1022.64	0.5776	0.1814	1436.31	1024.57
0.6540	0.1073	1475.84	1049.11	0.6656	0.0914	1485.78	1055.00
0.7550	0.0000	1527.10	1082.54	0.7550	0.0000	1537.10	1082.54
308.15 K							
0.0000	0.8017	1244.73	851.99	0.0000	0.7720	1130.52	807.40
0.0694	0.7281	1259.47	873.98	0.0787	0.6916	1170.84	836.73
0.1418	0.6511	1280.94	896.00	0.1586	0.6099	1208.68	867.87
0.2175	0.5707	1302.26	917.51	0.2397	0.5269	1239.73	900.76
0.2967	0.4866	1323.15	941.55	0.3222	0.4426	1271.84	928.58
0.3797	0.3985	1343.63	967.55	0.4060	0.3569	1314.94	956.71
0.4667	0.3061	1373.57	991.05	0.4911	0.2699	1355.63	982.76
0.5580	0.2092	1405.78	1016.41	0.5776	0.1814	1400.63	1010.25
0.6540	0.1073	1452.36	1042.27	0.6656	0.0914	1452.47	1041.62
0.7550	0.0000	1520.94	1072.32	0.7550	0.0000	1520.94	1072.32
313.15 K							
0.0000	0.8017	1222.10	844.94	0.0000	0.7720	1100.78	797.56
0.0694	0.7281	1240.78	867.13	0.0787	0.6916	1140.15	828.58
0.1418	0.6511	1259.47	890.54	0.1586	0.6099	1174.31	859.22
0.2175	0.5707	1278.05	913.25	0.2397	0.5269	1205.63	888.49
0.2967	0.4866	1302.47	938.04	0.3222	0.4426	1245.31	917.49
0.3797	0.3985	1326.47	962.23	0.4060	0.3569	1282.21	944.42
0.4667	0.3061	1353.21	985.44	0.4911	0.2699	1320.63	972.56
0.5580	0.2092	1391.05	1010.87	0.5776	0.1814	1370.84	1002.92
0.6540	0.1073	1442.10	1036.34	0.6656	0.0914	1422.63	1035.19
0.7550	0.0000	1511.47	1066.08	0.7550	0.0000	1511.47	1066.08
318.15 K							
0.0000	0.8017	1210.78	837.81	0.0000	0.7720	1078.94	784.04
0.0694	0.7281	1223.15	859.47	0.0787	0.6916	1110.52	815.65
0.1418	0.6511	1240.78	883.89	0.1586	0.6099	1145.36	845.76
0.2175	0.5707	1257.47	905.48	0.2397	0.5269	1176.31	875.03
0.2967	0.4866	1283.15	930.73	0.3222	0.4426	1206.15	902.22
0.3797	0.3985	1305.00	955.45	0.4060	0.3569	1242.00	930.61
0.4667	0.3061	1330.05	978.02	0.4911	0.2699	1285.00	961.34
0.5580	0.2092	1365.00	1003.74	0.5776	0.1814	1332.78	994.09
0.6540	0.1073	1424.94	1029.47	0.6656	0.0914	1395.36	1025.83
0.7550	0.0000	1505.10	1061.86	0.7550	0.0000	1505.10	1061.86

From table.1 it is observed that the ultrasonic velocity and density values increase non-linearly in two systems with the mole fraction of first component. This trend suggests the possibility of intermolecular interactions between the components of the mixtures. The increasing values of density shows that the addition of first component makes the system to be more compact, thereby showing the attractive type interactions between the components. As the medium becomes more and more compact, velocity also increases as is observed in this case.

The variations of V_m^E, u^E and Z^E with the mole fraction of quinoline for two systems at (303.15, 308.15, 313.15, 318.15) K are plotted in Figure 1(a, b), Figure 2(a,b) and Figure3(a,b) respectively.

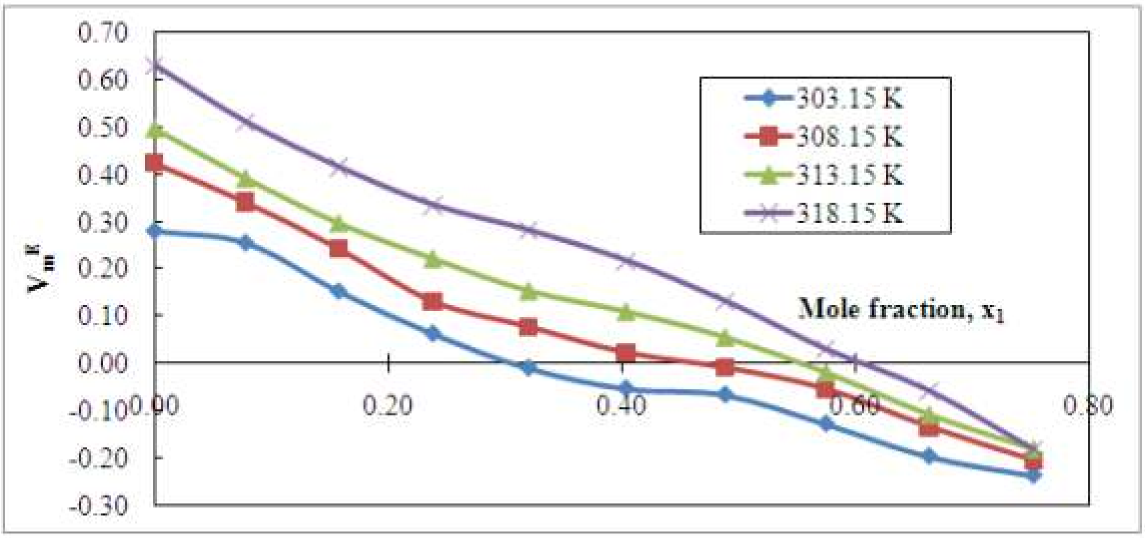

Figure 1(b): Variation of excess molar volume, V_m^E, with mole fraction, x_1, for Quinoline+ methanol+ toluene mixtures at different temperatures:♦,303.15K; ■,308.15K; ▲, 313.15K; and ×, 318.15K.

The results shown in Figures 1(a), 1(b) indicate that V_m^E values are positive at lower mole fractions and negative at higher mole fractions at all temperatures reported. Generally, dispersive forces and improper interstitial accommodation of molecules of a ternary mixture will be reflected in positive V_m^E[8,9]. However, strong interactions have taken place between unlike molecules through charge transfer forces.The formation of new hydrogen bonds and proper interstitial accommodation will yield negative V_m^E.

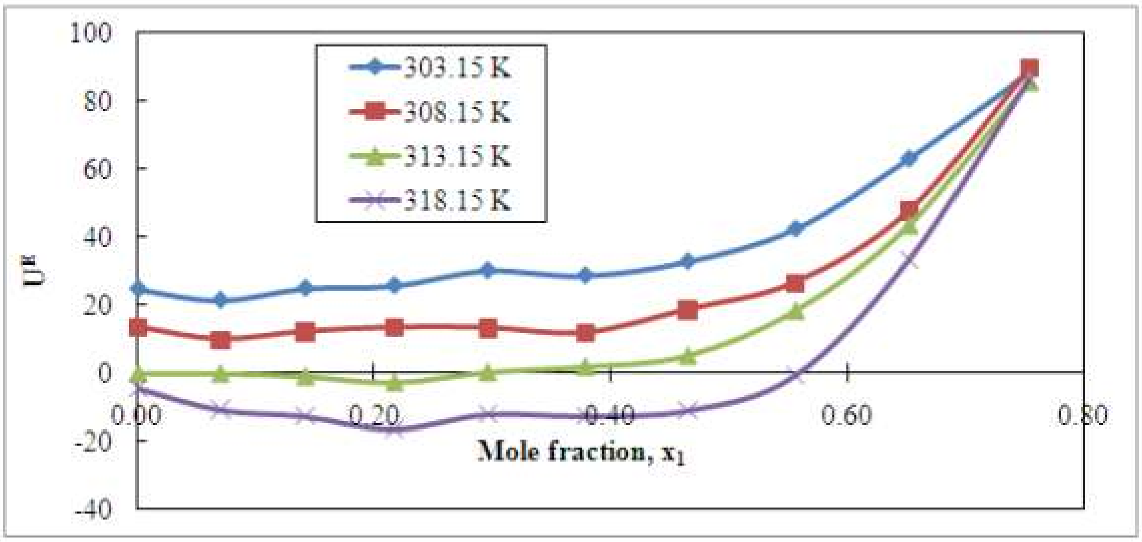

Figure 2(a): Variation of excess ultrasonic velocity, u^E, with mole fraction, x_1, for Quinoline+ methanol+benzene mixtures at different temperatures:♦,303.15K; ■,308.15K; ▲, 313.15K; and ×, 318.15K.

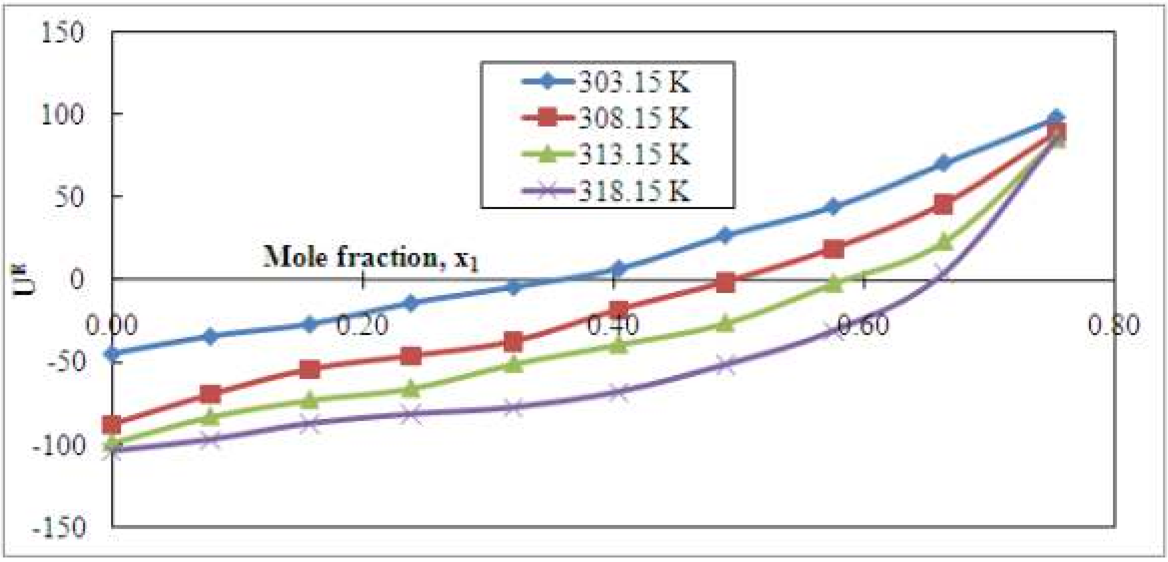

Figure 2(b): Variation of excess ultrasonic velocity, u^E, with mole fraction, x_1, for Quinoline+ methanol+ toluene mixtures at different temperatures:♦,303.15K; ■,308.15K; ▲, 313.15K; and ×, 318.15K.

From Figures 2(a), 2(b) it is observed that the mole fraction of quinoline increases the uE values and becomes more positive at all temperatures. For system-1, at lower temperature the UE values are positive and at higher temperature these values are observed to be negative. Whereas in system-2 the same trend is observed at all temperatures.The liquid mixture volume depends upon intermolecular interactions as well as structural arrangement10. An increase in the strength of the heteromolecular forces manifests a decrease in adiabatic compressibility and volume and, hence the size of cluster. Thus, negative VmE values account for the strong interactions between the unlike molecules. Thus excess molar volume and excess ultrasonic velocity complements the presence of strong interactions in the system and at lower mole fraction of quinoline.

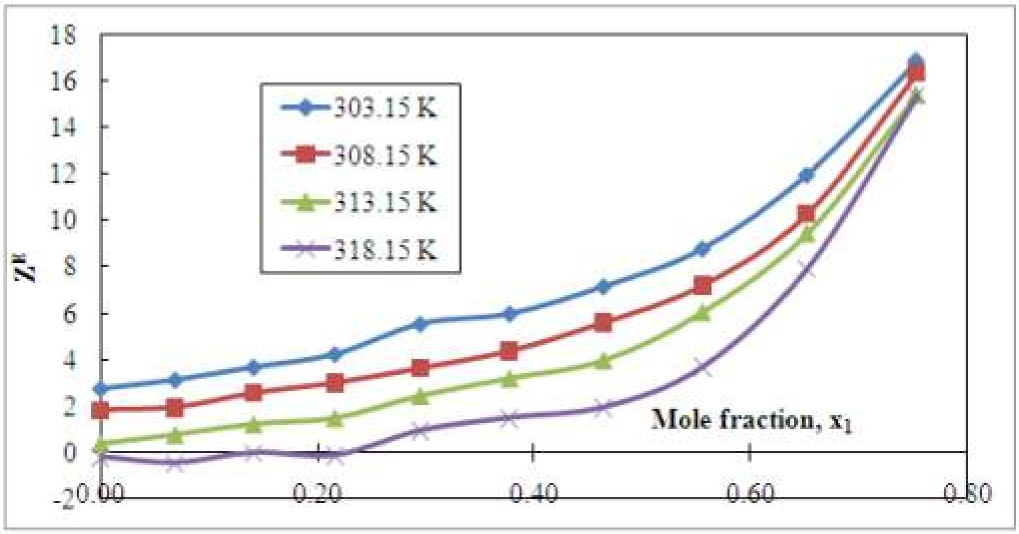

Figure 3(a): Variation of excess acoustic impedance, Z^E, with mole fraction, x_1, for Quinoline+ methanol+ benzene mixtures at different temperatures:♦,303.15K; ■,308.15K; ▲, 313.15K; and ×, 318.15K.

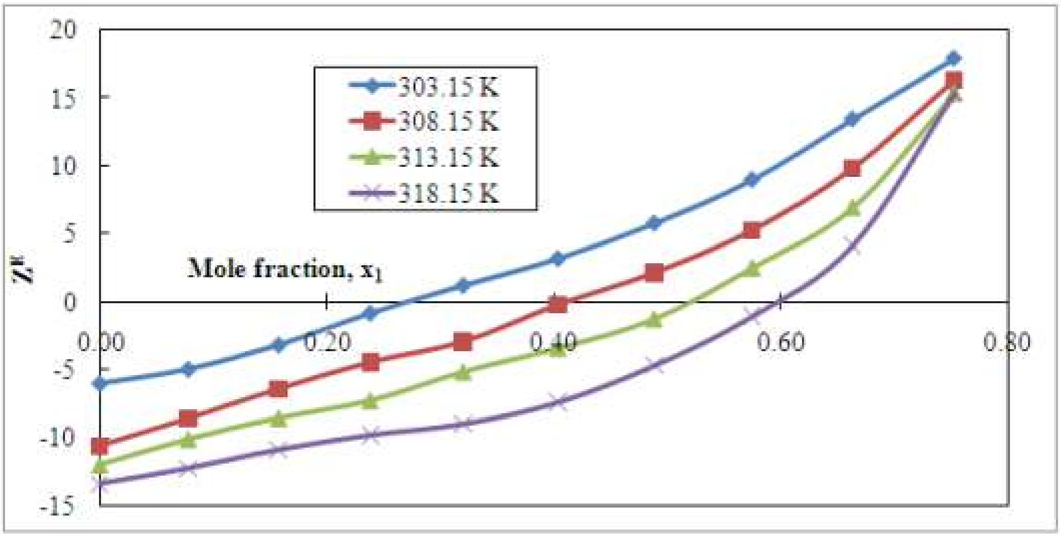

Figure 3(b): Variation of excess acoustic impedance, Z^E, with mole fraction, x_1, for Quinoline+ methanol+ toluene mixtures at different temperatures:♦,303.15K; ■,308.15K; ▲, 313.15K; and ×, 318.15K.

From Figures 3(a) it is observed that the excess acoustic impedance values are almost positive at all mole fractions of quinoline. For system-2, it is observed from figure 3(b) that the Z^E values are observed to be negative at lower mole fractions and positive at higher mole fractions. The positive deviations in UE from linear dependence suggest the presence of strong interactions between the component molecules11.

From all the above results we may conclude that there exist strong interactions between the molecules of the mixtures in the systems chosen for the study.

CONCLUSIONS

Ultrasonic velocity and density values are measured in pure components and ternary mixtures of quinoline + methanol + benzene andquinoline + methanol + toluene at temperatures 303.15, 308.15, 313.15 and 318.15 K over the entire composition range.The observed positive and negative values of V_m^E, u^E and Z^E suggest the presence of molecular interactions in the present system.

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