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Acoustical study on molecular interactions in binary liquid mixture at different temperatures

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ABSTRACT

Ultrasonic velocity (u), density (ρ), and viscosity (η) values have been measured experimentally in the binary liquid mixture containing quinoline and m-xylene at different temperatures 303.15K, 308.15K, 313.15K and 318.15K over the entire range of composition. This experimental data have been used to calculate the acoustical parameters such as adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π). The results have been qualitatively used to explain the molecular interactions between the components of the liquid mixture.

Keywords: Ultrasonic velocity, Quinoline, m-xylene, adiabatic compressibility, free volume.

INTRODUCTION

The Knowledge of acoustical parameters is of great importance in studying the molecular interactions and physicochemical behaviour in binary liquid mixtures [1,2].The study of molecular interactions in the liquid mixtures is of considerable in the elucidation of the structural properties of the molecules. The intermolecular interactions influence the structural arrangement along with the shape of the molecules. In the recent years, ultrasonic technique has been found to be one of the most powerful technique for studying the nature of molecular interactions in liquid mixtures. Acoustical parameters are used to understand different kinds of association, the molecular packing, molecular motion, physico-chemical behaviour and various types of intermolecular interactions and their strengths, influenced by the size in pure components and in the mixtures. As a part of Today's progressive and ongoing research [3,4] on thermodynamic and acoustic properties of binary liquid mixtures, we report here the results of study on binary mixture of quinoline and m-xylene over the ntire range of composition at T= 303.15K, 308.15K, 313.15K and 318.15K. By using these experimental values of ultrasonic velocity (u), density (ρ) and viscosity (η), acoustical parameters such as adiabatic compressibility, free length, free volume and internal pressure have been estimated using standard relations.

MATERIALS AND METHODS

All the liquids used were purified by standard procedure [5]. Job's method of continuous variation was used to prepare the mixtures in the required proportions. Job's method of continuous variation was used to prepare the mixtures of required proportions. The various concentrations are prepared by varying mole fractions. The prepared 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. The ultrasonic velocities were measured by using single crystal ultrasonic pulse echo interferometer (Mittal enterprises, India; Model: F-80X). It consists of a high frequency generator and a measuring cell. The measurements of ultrasonic velocities were made at a fixed frequency of 3MHz. The capacity of the measuring cell is 12ml.

The ultrasonic velocity has an accuracy of ± 0.5 $m.s^{-1}$. The temperature was controlled by circulating water around the liquid cell from thermostatically controlled constant temperature water bath (accuracy ± 0.01K).

The densities of pure liquids and liquid mixtures were measured by using a specific gravity bottle with an accuracy of ± 0.5%. An electronic balance (Shimadzu AUY220, Japan), with a precision of ±0.1 mg was used for the mass measurements. Averages of 4 to 5 measurements were taken for each sample.

Viscosities were measured at the desired temperature using Ostwald's viscometer, which was calibrated using water and benzene. The flow time has been measured after the attainment of bath temperature by each mixture. The flow measurements were made with an electronic stopwatch with a precision of 0.01 s. The viscosities η, were obtained from the following relation:

$\eta = k . \rho . t$ --- (1)

Where k, ρ and t, are viscometric constant, density of liquid and time of efflux for a constant volume of liquid respectively. For all pure compounds and mixtures, 4 to 5 measurements were performed and the average of these values was used in all calculations. The values are accurate to ± 0.001cP. The experimentally measured values of pure components are compared with the literature [6,7] values and are given in (Table 1).

Table 1: Experimental and literature values of density and ultrasonic velocity of pure liquids

Liquids	**Density(ρ) kgm^{-3}**		**Ultrasonic velocity(u) ms^{-1}**	
	Experimental	**Literature**	**Experimental**	**Literature**
Quinoline	1085.45	1085.79 (6)	1553.68	1547 (6)
m-xylene	855.70	855.47 (7)	1304.21	1300.34 (7)

Theory: From the experimentally measured values of ultrasonic velocity (u), density (ρ) and viscosity (η), various ultrasonic derivable parameters such as adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π) are calculated using the following equations:

$\beta = 1/\rho u^2$ --- (2)

$L_f = K_T\beta^{1/2}$ --- (3)

$V_f = Mu/\eta K$ --- (4)

$\pi = bRT (K\eta/u)(\rho^{2/3}/M^{7/6})$ --- (5)

where K_T is the temperature dependent constant, M is the effective molecular weight of the solution, K is the temperature independent constant ($K = 4.28 \times 10^9$), b a constant which is 2 for cubic packing, R the universal gas constant and T is the absolute temperature.

RESULTS AND DISCUSSION

The experimental values of density (ρ), viscosity (η) and ultrasonic velocity (u) for the binary liquid mixture over the entire range of composition at different temperatures 303.15K, 308.15K, 313.15K, 318.15 K are presented in (Table 2) . From (Table 2) it is observed that the ultrasonic velocity increases with increase in mole fraction of quinoline. This may be due to association of a very strong dipole-induced dipole interaction between the component molecules.

Table 2: Values of density (ρ), viscosity (η) and ultrasonic velocity (u) of liquid mixture at T = 303.15K, 308.15K, 313.15K and 318.15K

Molefraction (X)	ρ Kgm^{-3}	η$X10^{-3}$ Nsm^{-2}	u ms^{-1}	ρ Kgm^{-3}	η Nsm^{-2}	u ms^{-1}
Quinoline+m-xylene						
	T=303.15K			**T=308.15K**		
0.0000	855.70	0.554	1304.21	848.70	0.522	1285.27
0.1038	887.18	0.711	1375.05	880.54	0.761	1362.89
0.2067	913.84	0.803	1398.26	910.65	0.854	1384.79
0.3088	931.94	0.934	1420.05	925.52	0.983	1407.74
0.4100	952.56	0.990	1440.16	945.83	1.121	1428.68
0.5104	978.74	1.221	1461.95	974.27	1.260	1452.63
0.6099	998.14	1.507	1482.53	996.30	1.462	1474.35
0.7086	1014.85	1.948	1502.32	1011.43	1.782	1495.16
0.8066	1043.74	2.179	1521.42	1038.14	1.957	1516.79
0.9037	1066.84	2.660	1532.89	1062.01	2.325	1529.26
1.0000	1085.45	2.932	1553.68	1082.11	2.707	1550.68
	T=313.15K			**T=318.15K**		
0.0000	845.80	0.493	1266.32	840.50	0.468	1244.21
0.1038	875.63	0.572	1354.74	871.03	0.573	1345.26
0.2067	904.25	0.653	1373.68	900.75	0.628	1361.05
0.3088	921.60	0.724	1395.26	918.29	0.714	1382.63
0.4100	942.91	0.821	1418.37	940.30	0.811	1406.89
0.5104	969.91	0.983	1443.47	966.98	0.917	1432.84
0.6099	992.34	1.187	1466.89	989.29	1.123	1457.26
0.7086	1009.59	1.529	1488.84	1006.23	1.463	1479.89
0.8066	1034.56	1.740	1511.32	1031.79	1.701	1503.21
0.9037	1059.32	2.076	1525.79	1056.74	2.007	1519.47
1.0000	1078.60	2.447	1547.37	1074.99	2.430	1541.05

The calculated thermo acoustical parameters such as adiabatic compressibility(β), free length (L_f), free volume (V_f) and internal pressure (π) by using standard relations and are given in (Table 3)**.** The variations of these thermo acoustical parameters with the mole fraction of quinoline are also represented in the form of graphs from **(**Figure 1) to (Figure 4) respectively**.** Adiabatic compressibility is a measure of intermolecular association or dissociation or repulsion. It is independent of temperature and pressure for unassociated and weakly associated molecules. It also determines the orientation of the solvent molecules around the liquid molecules. The structural arrangement of the molecule affects the adiabatic compressibility. From (Table 3) and (Figure 1) , it is observed that adiabatic compressibility decreases with increase in mole fraction of quinoline in the mixture taken up for study. As adiabatic compressibility is inversely proportional to ultrasonic velocity, since ultrasonic velocity increases with mole fraction, so that adiabatic compressibility decreases with mole fraction of quinoline.

Table 3: Values of adiabatic compressibility(β), intermolecular free length(L_f), free volume(V_f) and internal pressure(π) of liquid mixture at T = 303.15K, 308.15K, 313.15K and 318.15K

Molefraction (X)	**β X10^{-11} Kg^{-1} m s^2**	**L_f A^O**	**V_fX10^{-7} m^3**	**π X10^6 atm**	**β X10^{-11} Kg^{-1} m s^2**	**L_f A^O**	**V_fX10^{-7} m^3**	**π X10^6 Atm**
Quinoline+m-xylene								
	T=303.15K				**T=308.15K**			
0.0000	68.7042	0.0164	4.4471	261.38	71.3275	0.0169	4.7496	254.31
0.1038	65.5344	0.0160	3.4275	287.73	67.9131	0.0164	3.0510	297.62
0.2067	62.3913	0.0156	3.0258	301.54	64.5273	0.0159	2.7157	311.88
0.3088	59.2744	0.0151	2.5455	319.14	61.1698	0.0155	2.3264	327.35
0.4100	56.1834	0.0147	2.4589	323.17	57.8403	0.0150	2.0149	343.72
0.5104	53.1181	0.0143	1.8906	354.48	54.5384	0.0146	1.7852	360.22
0.6099	50.0781	0.0139	1.4489	387.45	51.2637	0.0141	1.5034	382.24
0.7086	47.0631	0.0135	1.0343	432.91	48.0160	0.0137	1.1733	414.16
0.8066	44.0728	0.0131	0.9161	453.74	44.7948	0.0132	1.0709	429.19
0.9037	41.1068	0.0127	0.7054	496.40	41.6000	0.0128	0.8598	463.30
1.0000	38.1650	0.0122	0.6384	513.20	38.4310	0.0124	0.7173	492.61
	T=313.15K				**T=318.15K**			
0.0000	73.7302	0.0173	5.0708	248.26	76.8555	0.0178	5.3359	243.06
0.1038	70.0965	0.0168	4.6405	257.83	72.9441	0.0172	4.5785	258.08
0.2067	66.4933	0.0163	4.0201	272.37	69.0655	0.0167	4.1975	267.79
0.3088	62.9203	0.0158	3.6363	281.27	65.2193	0.0162	3.6632	279.90
0.4100	59.3770	0.0153	3.1784	294.66	61.4051	0.0157	3.1982	293.51
0.5104	55.8630	0.0148	2.5691	318.11	57.6226	0.0152	2.8172	307.86
0.6099	52.3781	0.0144	2.0395	344.37	53.8713	0.0147	2.1960	335.31
0.7086	48.9218	0.0139	1.4678	383.90	50.1509	0.0142	1.5545	375.79
0.8066	45.4938	0.0134	1.2712	404.41	46.4609	0.0137	1.3037	400.31
0.9037	42.0938	0.0130	1.0160	437.49	42.8010	0.0132	1.0621	430.37
1.0000	38.7214	0.0125	0.8321	467.82	39.1708	0.0127	0.8355	466.14

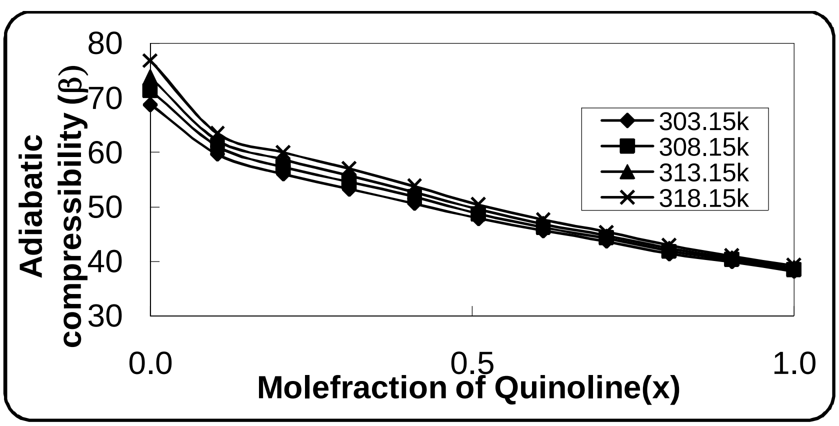

Figure 1: Variation of adiabatic compressibility with molefraction of quinoline.

From (Table 3) and (Figure 2), it is observed that free length also decreases with increase in mole fraction of quinoline.The free length is the distance between the surfaces of the neighboring molecules. Generally, when the ultrasonic velocity increases, the value of the free length decreases.

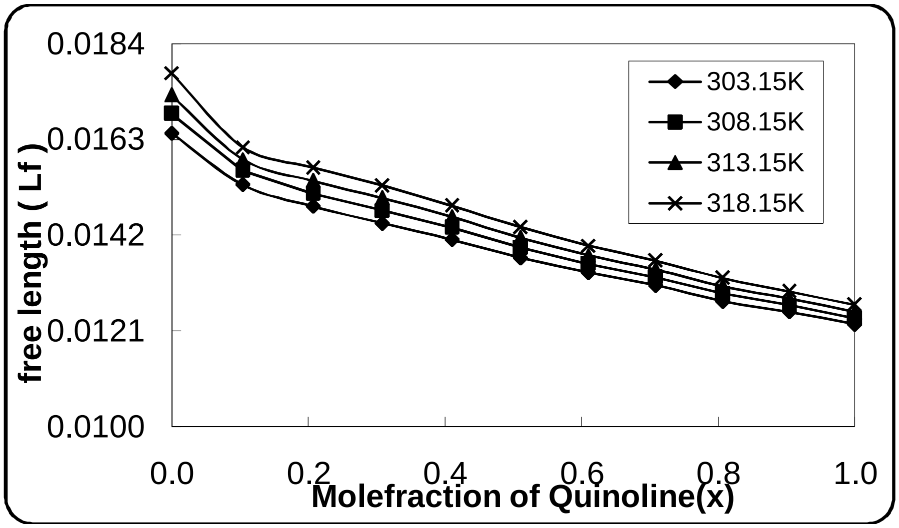

Figure 2: Variation of free length with molefraction of quinoline.

The observed increase in ultrasonic velocity and corresponding decrease in free length with mole fraction of quinoline in the binary liquid mixture is in accordance with the proposed by [9]. From (Table 3) it is studied that the values of adiabatic compressibility and free length increases with increase in temperatures, it clearly reveals that interaction become stronger at lower temperatures. Similar variations are observed in case of free volume (Table 3) and it is represented in (Figure 3).

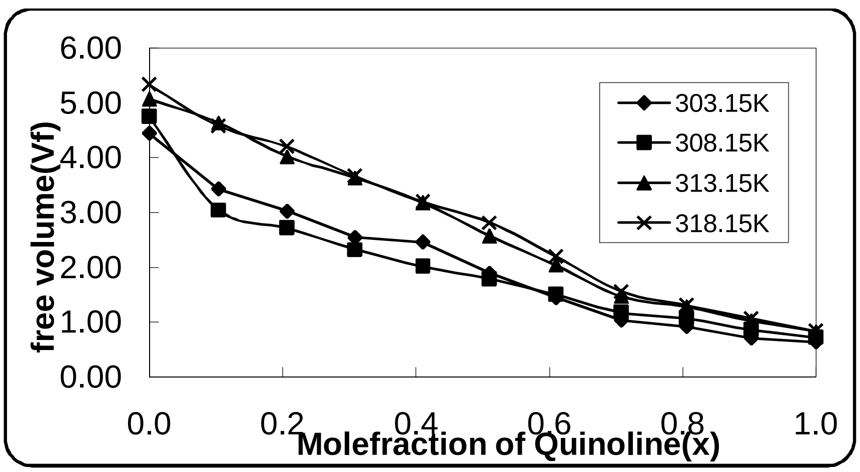

Figure 3: Variation of free volume with molefraction of quinoline.

Free volume is defined as the average volume in which the centre of the molecules can move inside the hypothetical cell due to the repulsion of surrounding molecules. Also it is observed from (Table3) and (Figure 4) that internal pressure increases with increase in mole fraction of quinoline.

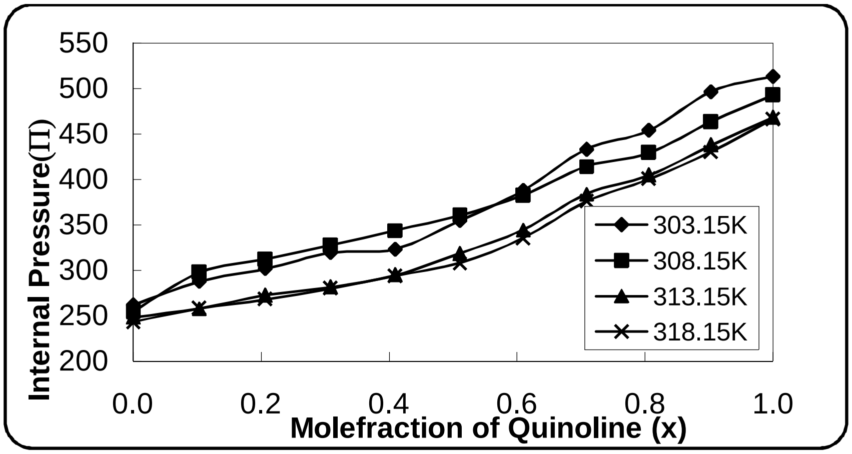

Figure 4: Variation of internal pressure with molefraction of quinoline

Internal pressure is a fundamental property of a liquid, which provides an excellent basis for examining the solution phenomenon and studying various properties of the liquid state. It is a measure of the change in the internal energy of liquid or liquid mixtures, as it undergoes a very small isothermal change. It is a measure of cohesive or binding forces between the solute and solvent molecules. Internal pressure is a fundamental property of a liquid, which provides an excellent basis for examining the solution phenomenon and studying various properties of the liquid state. It is a measure of the change in the internal energy of liquid or liquid mixtures, as it undergoes a very small isothermal change. It is a measure of cohesive or binding forces between the solute and solvent molecules.

APPLICATION

Xylene is widely used in the areas of application include printing, rubber, and leather industries with sweet smelling. Similarly it is a cleaning agent. Quinoline is a colorless liquid with strong odor and widely used in manufacturing of dyes, pesticides and solvent for resins and terpenes.

CONCLUSIONS

It is very obvious from values of ultrasonic velocity, density, viscosity and calculated acoustical parameter of the binary liquid mixture containing quinoline and m-xylene at 303.15K, 308.15K, 313.15K and 318.15K that there exists a strong molecular association between the components of the liquid mixture.

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