



Molecular Interactions in Ternary Liquid Mixtures at different Temperatures – An Ultrasonic Study

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ABSTRACT

Ultrasonic velocity, density and viscosity have been measured in pure Quinoline, o-xylene and methanol and in their ternary liquid mixtures with methanol as common compound at temperatures 303.15, 308.15, 313.15 and 318.15 K over the entire composition range. From these experimental values various parameters like adiabatic compressibility, free volume, intermolecular free length and internal pressure and their excess values have been evaluated. The excess parameters were plotted against the mole fraction of quinoline over the whole composition range. The observed negative and positive values of excess parameters were explained on the basis of intermolecular interactions present in these mixtures.

Keywords: o-xylene, quinoline, ultrasonic speed, viscosity, density.

INTRODUCTION

During the last two decades, ultrasonic study of liquid and liquid mixtures has gained much importance in assessing the nature of molecular interactions and investigating the physicochemical behavior of such systems[1]. Literature survey[2,3] reveals that excess values of thermo acoustical parameters are useful in understanding the interactions between the molecules. The systematic investigation of excess properties are therefore of great importance. The present investigation is a study of temperature variation of ultrasonic velocity, density, viscosity, excess adiabatic compressibility, β^E , excess free volume, V^E , excess intermolecular free length, L_f^E and excess internal pressure, π^E in quinoline + methanol+o-xylene.

MATERIALS AND METHODS

Materials: The mass fractions of Quinoline, methanol and o-xylene obtained from SDFCL are 0.98, 0.99 and 0.90 respectively. All the liquids obtained from the suppliers were further purified by standard procedure[4]. A comparison of the experimental values of density, viscosity and ultrasonic velocity obtained in the present study with the values reported in literature shows good agreement.

Procedure: To prepare the mixtures in required proportions, Job's method of continuous variation was used. Well-stoppered conical flasks were used to preserve the mixtures. After thorough mixing of the

liquids, the flasks were left undisturbed to allow them to attain thermal equilibrium. An electronic balance (Shimadzu AUY220 from Japan), with a precision of ± 0.1 mg was used for the mass measurements. The densities of pure liquids and liquid mixtures were measured by using a specific gravity bottle with an accuracy of $\pm 10^{-4}$ g/cm³.

Viscosities were measured at desired temperature using Ostwald's viscometer. 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. For all pure compounds and mixtures, 5 to 7 measurements were performed and the average of these values was used in all calculations. The values are accurate to $\pm 10^{-3}$ mPaS. A single crystal ultrasonic pulse echo interferometer (Model: F-80X Mittal enterprises, India) is used for measuring ultrasonic velocities. The measurements of ultrasonic velocities were made at a fixed frequency of 3 MHz. The equipment was calibrated by measuring the velocity in carbon tetrachloride and benzene. The results are in good agreement with those reported in literature[5]. The error in velocity measurement is ± 0.5 %. The temperature was controlled through water circulation around the liquid cell using thermostatically controlled constant temperature water bath with an accuracy of ± 0.01 K.

From the experimental values of ultrasonic velocity, density and viscosity, various parameters are evaluated using the standard equations[6]. The strength of interaction between the component molecules of the binary mixtures is well reflected in the deviation of the excess functions from ideality. The excess properties such as β^E , V^E , L_f^E and π^E have been calculated using the equation

$$Y^E = Y_{\text{mix}} - [x_1 Y_1 + x_2 Y_2 + x_3 Y_3] \quad (1)$$

Where Y^E is β^E , V^E , L_f^E or π^E and x represent mole fraction of the component and subscript 1, 2 and 3 for the components 1, 2 and 3 respectively.

RESULTS AND DISCUSSION

The ultrasonic velocity (u), density (ρ) and viscosity (η) values of ternary mixture at 303.15, 308.15, 313.15 and 318.15 K are given in table 1. From these observed values various acoustical parameters like adiabatic compressibility (β), free volume (V), free length (L_f) and internal pressure (π) have been evaluated and is presented in table 2.

Table-1. Ultrasonic velocity, density and viscosity of ternary liquid mixtures at different temperatures.

x_1	u (ms ⁻¹)	ρ (Kg m ⁻³)	$\eta \times 10^{-3}$ (NSm ⁻²)	u (ms ⁻¹)	ρ (Kg m ⁻³)	$\eta \times 10^{-3}$ (NSm ⁻²)
	303.15 K			308.15 K		
0.0000	1301.05	919.47	0.7478	1282.10	913.82	0.6573
0.0850	1322.63	940.38	0.8875	1307.36	933.27	0.8140
0.1697	1344.73	971.65	0.9990	1332.63	964.69	0.9328
0.2541	1370.63	992.66	1.1614	1356.73	986.38	1.0572
0.3381	1392.36	1024.54	1.3521	1380.68	1018.81	1.2058
0.4217	1412.89	1046.06	1.5224	1400.78	1040.16	1.3546
0.5050	1432.63	1064.03	1.7688	1420.63	1057.96	1.5681
0.5880	1452.00	1090.22	2.0918	1442.42	1085.19	1.8024

0.6706	1471.57	1107.58	2.5350	1459.84	1101.20	2.0952
0.7530	1491.05	1125.04	3.0203	1480.52	1120.25	2.5021
	313.15 K			318.15 K		
0.0000	1266.84	907.07	0.5802	1256.84	900.24	0.5080
0.0850	1292.78	926.52	0.7048	1276.84	919.37	0.5856
0.1697	1318.15	957.51	0.8002	1297.89	952.57	0.6539
0.2541	1338.42	979.79	0.9133	1322.63	972.61	0.7646
0.3381	1361.05	1013.52	1.0222	1343.69	1009.05	0.8834
0.4217	1380.00	1034.13	1.1807	1361.57	1027.21	1.0082
0.5050	1400.52	1050.84	1.3109	1382.10	1045.85	1.1502
0.5880	1423.47	1078.95	1.5415	1400.00	1073.12	1.3542
0.6706	1443.68	1096.16	1.7802	1421.84	1089.21	1.5397
0.7530	1467.89	1113.28	2.0207	1447.36	1110.27	1.7428

Table-2. Adiabatic compressibility, free volume, free length and internal pressure of ternary liquid mixtures at different temperatures.

x_1	x_3	β ($\times 10^{-11} \text{ m}^2 \text{ N}^{-1}$)				V ($\text{m}^3 \text{ mol}^{-1}$)			
		303.15	308.15	313.15	318.15	303.15	308.15	313.15	318.15
0.0000	0.7484	64.2505	66.5729	68.6933	70.3207	671.05	796.62	943.51	1137.80
0.0850	0.6639	60.7884	62.6903	64.5798	66.7172	550.29	615.63	751.32	973.84
0.1697	0.5797	56.9143	58.3704	60.1072	62.3202	488.17	533.69	660.82	874.09
0.2541	0.4959	53.6239	55.0769	56.9746	58.7740	413.79	469.23	572.54	734.26
0.3381	0.4124	50.3464	51.4899	53.2623	54.8901	347.98	407.99	511.65	624.70
0.4217	0.3292	47.8880	48.9961	50.7768	52.5125	306.95	361.03	433.81	538.82
0.5050	0.2464	45.7908	46.8347	48.5161	50.0555	257.82	304.98	390.57	465.87
0.5880	0.1639	43.5063	44.2906	45.7408	47.5441	210.58	260.69	323.11	382.76
0.6706	0.0818	41.6929	42.6111	43.7706	45.4136	165.69	217.88	273.59	332.45
0.7530	0.0000	39.9803	40.7245	41.6877	42.9952	133.60	175.31	238.47	291.51
		L_f (m)				π (Nm^{-2})			
0.0000	0.7484	0.01589	0.01629	0.01667	0.01698	1282.00	1205.79	1134.04	1060.06
0.0850	0.6639	0.01546	0.01581	0.01616	0.01654	1369.63	1312.69	1222.43	1115.39
0.1697	0.5797	0.01496	0.01526	0.01559	0.01599	1435.69	1386.99	1285.23	1166.78
0.2541	0.4959	0.01452	0.01482	0.01518	0.01553	1517.03	1448.62	1349.62	1236.13
0.3381	0.4124	0.01407	0.01433	0.01468	0.01501	1618.78	1529.44	1413.35	1318.47
0.4217	0.3292	0.01372	0.01398	0.01433	0.01468	1688.43	1593.49	1493.08	1382.79
0.5050	0.2464	0.01342	0.01367	0.01401	0.01433	1786.15	1682.45	1542.32	1449.69
0.5880	0.1639	0.01308	0.01329	0.01360	0.01397	1917.09	1779.92	1650.65	1554.39
0.6706	0.0818	0.01280	0.01304	0.01331	0.01365	2072.24	1884.20	1741.16	1624.76
0.7530	0.0000	0.01254	0.01274	0.01299	0.01328	2222.12	2023.95	1819.07	1698.21

From table 1 it is observed that, the values of u , ρ and η increase with increasing molar concentration of quinoline. Quinoline is a colourless liquid with strong odor and widely used in the manufacturing of dyes, pesticides and solvent for resins. Xylene is widely used in the area of application including printing, rubber and leather industries with sweet smelling and as a cleaning agent. From table 2 it is observed that the adiabatic compressibility β is found to be decreased with increasing concentration of quinoline. It is primarily the compressibility that changes with structure which leads to change in ultrasonic velocity. The change in adiabatic compressibility in liquid mixtures indicates there is a definite contraction on mixing

and the variation is may be due to complex formation. This clearly shows that there is significant interaction between quionoline –xylene molecules[7].

Intermolecular free length shows a similar behaviour as reflected by adiabatic compressibility. Intermolecular free length is a predominant factor in determining the variation of ultrasonic velocity in the mixtures. The decrease in the values of adiabatic compressibility and the free length with increase in ultrasonic velocity further strengthens the strong molecular association[8] between unlike molecules. It is also observed from table 2 that the values of free volume decrease and internal pressure increase. Further, the decrease in free volume and increase in internal pressure with increase in concentration of quinoline clearly shows the increasing magnitude of interactions[9].

To understand the nature of molecular interactions between the components of the liquid mixtures, it is of interest to discuss the same in terms of excess parameters rather than actual values. Non-ideal liquid mixtures show considerable deviation from linearity in their physical behaviour with respect to concentration and these have been interpreted on the basis of strong or weak interactions. The negative excess values are due to dipole-dipole, dipole-induced dipole, charge transfer interaction and hydrogen bonding between unlike molecules whereas the positive excess values are due to dispersive forces[10].

In the present investigation, the excess adiabatic compressibility (figure 1), the excess free length (figure 2) and excess free volume (figure 3) exhibit negative values at higher concentration of quinoline indicating the presence of strong interactions between unlike molecules. The strength of interaction between the component molecules increase, when excess values tend to become increasingly negative. This also may be quantitatively interpreted in terms of closer approach of unlike molecules leading to reduction in compressibility and volume¹¹. Further, the negative excess values of internal pressure (figure 4) supports the presence of strong molecular interactions between unlike molecules.

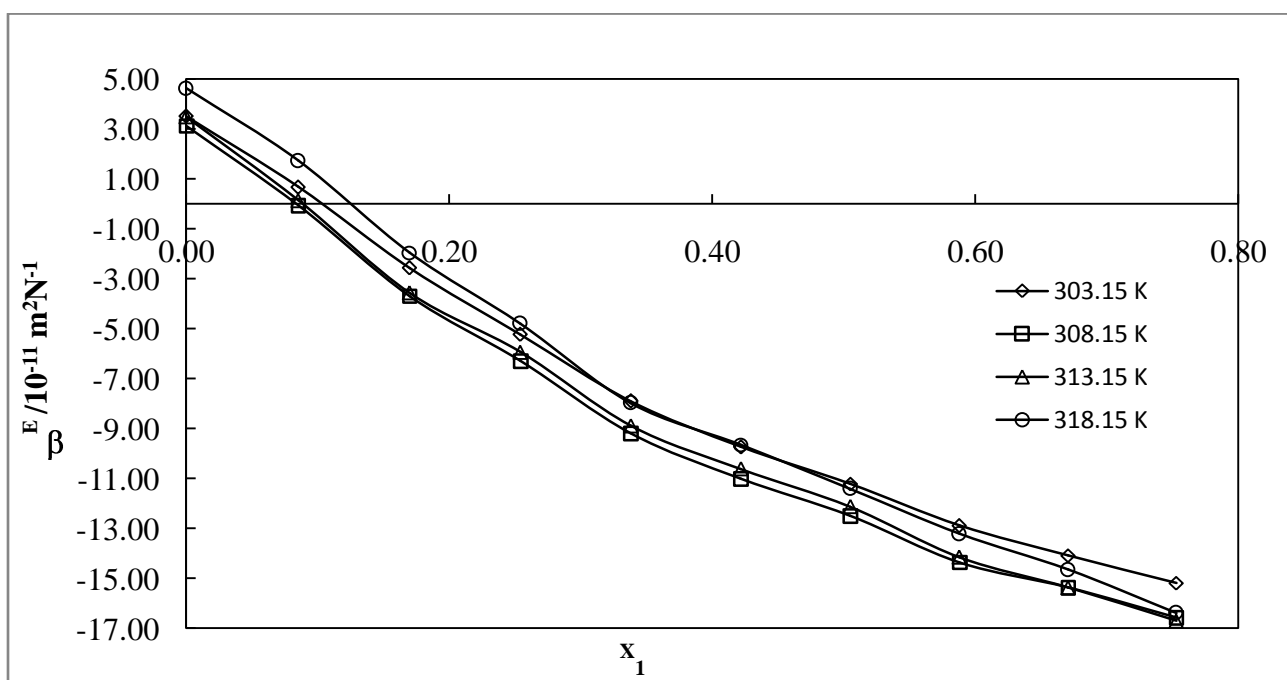


Figure 1: Variation of excess adiabatic compressibility with mole fraction of quinoline at different temperatures.

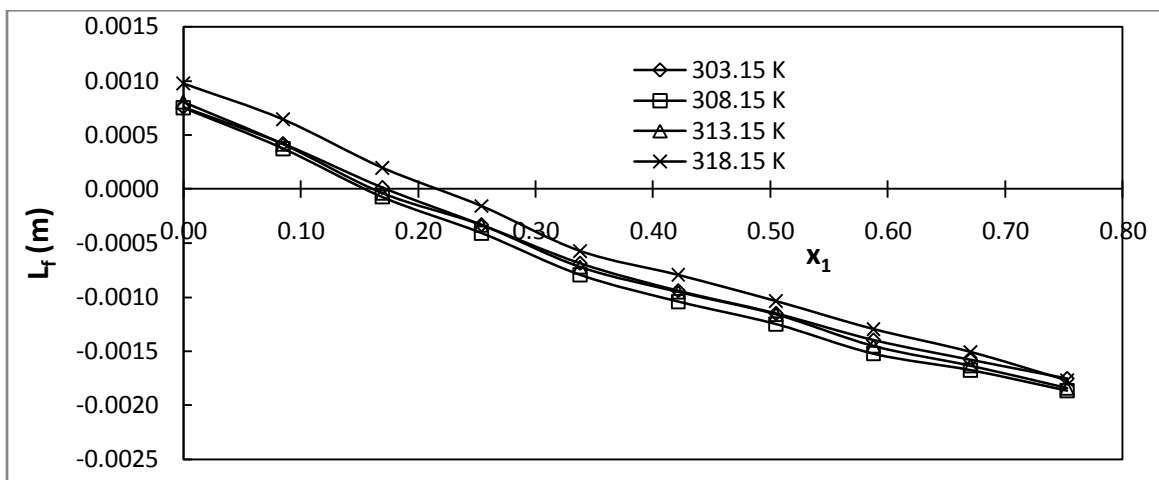


Figure 2: Variation of excess free length with mole fraction of quinoline at different temperatures.

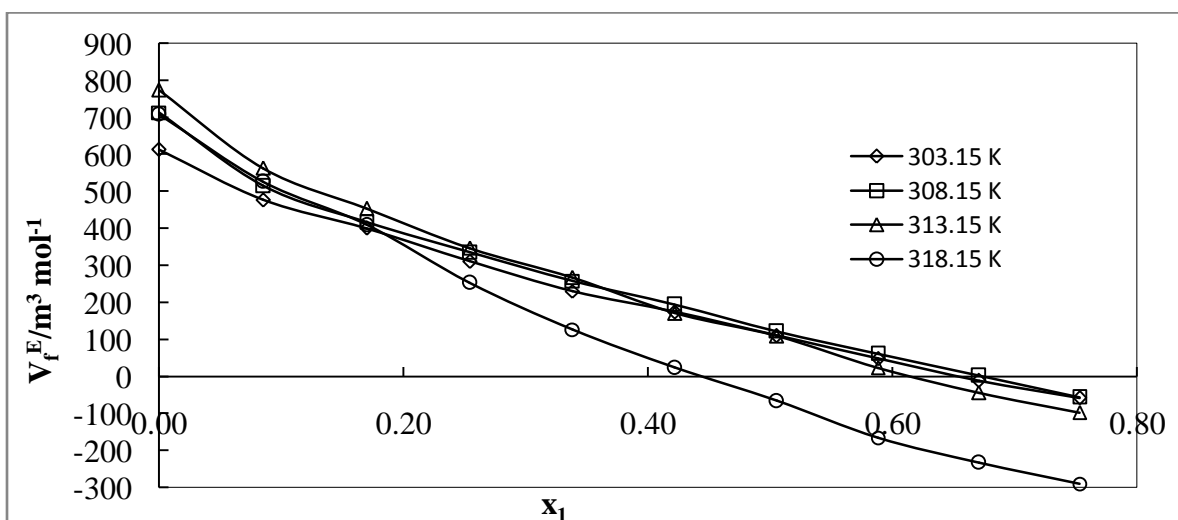


Figure 3: Variation of excess free volume with mole fraction of quinoline at different temperatures.

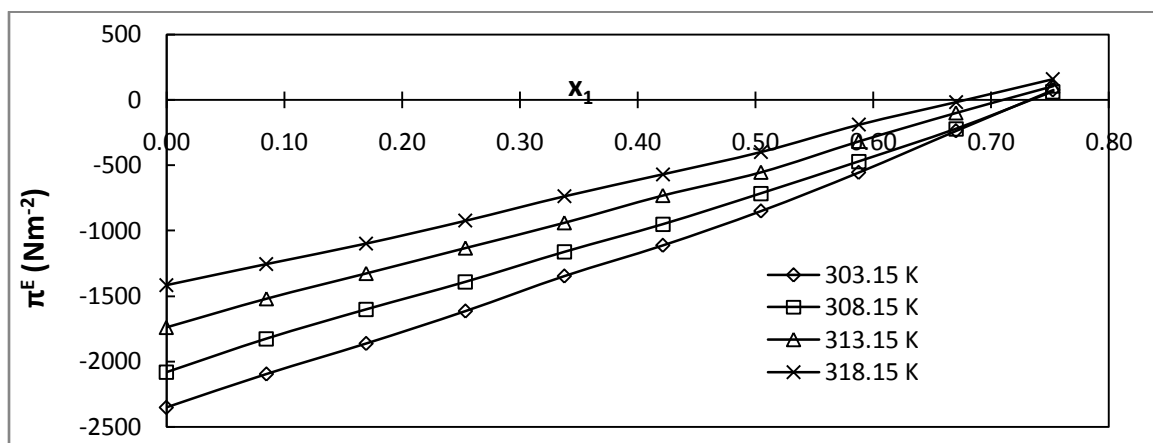


Figure 4: Variation of excess internal pressure with mole fraction of quinoline at different temperatures.

APPLICATIONS

From the results are useful to evaluate various parameters like adiabatic compressibility, free volume, intermolecular free length and internal pressure and their excess values.

CONCLUSIONS

From the data of ultrasonic velocity, density and viscosity various acoustic parameters and their excess parameters for the ternary liquid mixtures of quinoline with o-xylene in methanol at 303.15, 308.15, 313.15 and 318.15 K are calculated. It is observed from the results that there exist strong molecular interaction between the unlike molecules.

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