

STUDY OF EXCESS THERMOACOUSTICAL PARAMETERS IN BINARY LIQUID MIXTURES OF QUINOLINE WITH MESITYLENE AT TEMPERATURES T= (303.15, 308.15, 313.15 AND 318.15) K

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ABSTRACT

Ultrasonic velocities (u), Densities (ρ), and viscosities (η) have been measured in binary liquid mixtures of quinoline with mesitylene at temperatures $T = (303.15, 308.15, 313.15 \text{ and } 318.15) \text{ K}$ over the entire mole fraction range of quinoline. From the experimentally measured data, excess thermoacoustical parameters such as excess intermolecular free length (L_f^E), excess adiabatic compressibility (β^E), excess free volume (V_f^E) and excess enthalpy (H^E) have been calculated. These results are fitted to the Redlich-Kister polynomial equation. These results have been explained on the basis of intermolecular interactions present between the component molecules of the liquid mixtures.

Keywords: ultrasonic velocity, excess intermolecular free length, excess adiabatic compressibility, quinoline, mesitylene.

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INTRODUCTION

Study of excess thermoacoustical parameters is most important information in studying the strength of the molecular interactions in binary liquid mixtures^{1,2}. The study of molecular interactions in the liquid mixtures is of considerable elucidation of the structural properties of the molecules. The intermolecular interactions influence the structural arrangement and shape of the molecules. Ultrasonic velocity and their derived investigations in liquid mixtures find eminent applications in characterizing physico-chemical behavior and non-ideal behavior^{3,4}. As a part of ongoing research work^{5,6} authors in the present study reported the variations of excess thermoacoustical parameters such as excess intermolecular free length (L_f^E), excess adiabatic compressibility (β^E), excess free volume (V_f^E) and excess enthalpy (H^E) in binary liquid mixtures of quinoline with mesitylene at temperatures $T = (303.15, 308.15, 313.15 \text{ and } 318.15) \text{ K}$ over the entire mole fraction range of quinoline. The deviations of the excess parameters indicate the presence of interactions between the component molecules of the liquid mixtures.

EXPERIMENTAL

In the present investigation the chemicals used are of AR grade (Quinoline from SDFCL chemical distribution company with 98% of purity, Mesitylene from MERCK chemical distribution company with 99% of purity respectively) and they are purified by standard procedure. The different concentrations of the liquid mixture are prepared by varying mole fractions with respect to Job's method of continuous variation. Stoppard conical flasks are used for preserving the prepared mixtures and the flasks are left undisturbed to attain thermal equilibrium. Ultrasonic pulse echo interferometer (Mittal enterprises, India) is used for ultrasonic velocities measurements and all these measurements are done at a fixed frequency of 3MHz. The temperature of the pure liquids or liquid mixtures is done

by using temperature controlled water bath by circulating water around the liquid cell which is present in interferometer. Specific gravity bottle is used for the measurement of densities of pure liquids and liquid mixtures. An electronic weighing balance (Shimadzu AUY220, Japan), with a precision of + or - 0.1 mg is used for the measurements of mass of pure liquids or liquid mixtures. Average of 4 to 5 measurements is taken for each sample. Ostwald's viscometer is used for the measurement of viscosity of pure liquids or liquid mixtures. The time of flow of liquid in the viscometer is measured with an electronic stopwatch with a precision of 0.01s.

Theory

Excess thermoacoustical parameters are evaluated by using the equations given by Oswal *et al.*¹, Narendra *et al.*^{2,3} and Kumar *et al.*⁷.

$$\beta^E = \beta_{\text{exp}} - (x_1\beta_1 + x_2\beta_2) \text{ m}^2\text{N}^{-1} \quad (1)$$

$$L_r^E = L_r(\text{exp}) - (x_1L_{r1} + x_2L_{r2}) \text{ \AA} \quad (2)$$

$$V_f^E = V_{f(\text{exp})} - (x_1V_{f1} + x_2V_{f2}) \text{ m}^3 \text{ mol}^{-1} \quad (3)$$

$$H^E = H_{\text{exp}} - (x_1H_1 + x_2H_2) \text{ J mol}^{-1} \quad (4)$$

Where, β^E , L_r^E , V_f^E and H^E are the excess values of thermodynamical parameters such as adiabatic compressibility, intermolecular free length, free volume and enthalpy respectively. Here x is the mole fraction and 1, 2 represent 1st and 2nd component respectively.

The excess parameters are fitted to the following Redlich-Kister equation as given by Kumar *et al.*⁷.

$$A^E = x_1(1-x_1) - \sum_{i=1}^N A_i(2x_2-1)^i \quad (5)$$

RESULTS AND DISCUSSION

The sample provenance and purity are listed in the Table-1 and the comparison of experimentally measured values of densities, ultrasonic velocities and viscosities of pure liquids together with the literature values is given in Table-2. The experimentally measured values of ultrasonic velocities (u), densities (ρ) and viscosities (η) over entire mole fraction range of quinoline at temperatures $T=(303.15, 308.15, 313.15$ and $318.15)\text{K}$ are given in the Table-3.

Table-1: Details of liquid source, initial purity, purification method, final purity and analysis method

Liquid	Source	Initial purity	Purification method	Final purity	Analysis method
Quinoline	SDFCL	0.98	Fractional distillation	0.992	GC
Mesitylene	Merck	0.99	Fractional distillation	0.998	GC

GC-Gas Chromatography

Table-2: The values of densities (ρ), ultrasonic velocities (u) and viscosities (η) of pure liquids together with literature values at temperature $T=303.15\text{K}$.

Liquid	$\rho / (\text{Kg.m}^{-3})$		$u / (\text{m.s}^{-1})$		$\eta / (\text{Ns.m}^{-2})$	
	Exp	Lit	Exp	Lit	Exp	Lit
Quinoline	1085.5	1085.8 ⁸	1553.7	1547 ⁸	2.9320	2.9280 ⁸
Mesitylene	856.3	856.9 ⁹	1314.15	1316.82 ⁹	0.6213	0.6218 ⁹

Standard uncertainties (U_c) are given below:

$$U_c(u) = + \text{ or } - 0.1 \text{ m.s}^{-1}$$

$$U_c(\rho) = + \text{ or } - 0.01 \text{ Kg.m}^{-3}$$

$$U_c(\eta) = + \text{ or } - 0.001 \text{ Ns.m}^{-2}$$

Table-3: The values of ultrasonic velocities (u), densities (ρ) and viscosities (η) over entire molefraction range of quinoline at temperatures T= (303.15, 308.15, 313.15 and 318.15) K.

Mole fraction of quinoline (X_1)	Ultrasonic velocity(u)/(m.s ⁻¹)			
	T=303.15K	T=308.15K	T=313.15K	T=318.15K
0.0000	1314.15	1298.99	1282.65	1266.42
0.1160	1340.26	1324.15	1308.16	1292.04
0.2280	1369.37	1353.26	1337.27	1321.15
0.3361	1399.48	1383.37	1367.38	1351.26
0.4405	1427.59	1411.48	1395.49	1379.37
0.5415	1452.7	1436.59	1420.60	1404.48
0.6392	1476.81	1460.7	1444.71	1428.59
0.7337	1500.92	1483.81	1467.82	1452.70
0.8253	1523.03	1506.92	1491.93	1477.81
0.9140	1541.14	1528.03	1517.04	1505.92
1.0000	1553.68	1550.68	1547.37	1541.05
	Density(ρ)/(Kg.m ⁻³)			
0.0000	856.3	846.41	835.57	824.12
0.1160	878.23	868.34	857.50	846.05
0.2280	901.2	891.31	880.47	869.02
0.3361	922.2	912.31	901.47	890.02
0.4405	943.4	933.51	922.67	911.22
0.5415	956.4	946.51	935.67	924.22
0.6392	974.2	964.31	953.47	942.02
0.7337	989.67	979.78	968.94	957.49
0.8253	1002.9	993.01	982.17	970.72
0.9140	1029.2	1019.31	1008.47	997.02
1.0000	1085.4	1082.10	1078.60	1074.90
	viscosity (η)/(Ns.m ⁻²)			
0.0000	0.6213	0.5193	0.4053	0.2783
0.1160	0.9089	0.8102	0.7112	0.6102
0.2280	1.2002	1.0980	0.9801	0.8890
0.3361	1.4719	1.3593	1.2268	1.1413
0.4405	1.7314	1.6024	1.4583	1.3699
0.5415	1.9700	1.8340	1.6755	1.5840
0.6392	2.2010	2.0550	1.8777	1.7880
0.7337	2.4140	2.2580	2.0744	1.9789
0.8253	2.6148	2.4448	2.2504	2.1599
0.9140	2.7950	2.6150	2.4013	2.3103
1.0000	2.9318	2.7072	2.4400	2.3300

The excess thermodynamical parameters play an important role in studying the nature of molecular interactions in liquid mixtures¹⁰. The variations of the above excess thermoacoustical parameters such as excess intermolecular free length (L_f^E), excess adiabatic compressibility (β^E), excess free volume (V_f^E) and excess enthalpy (H^E) with the mole fractions of quinoline at temperatures T=(303.15,308.15,313.15 and 318.15)K are represented in the figures from Fig-1 to Fig-4 respectively

The variations of excess intermolecular free length (L_f^E) with the mole fraction of quinoline ranging from 0 to 1 at different temperatures in the present binary liquid mixtures are as shown in Fig-1. It is observed from Fig-1 is that, the excess intermolecular free length values are negative up to 0.5 mole fraction range and positive above 0.5 mole fraction range of quinoline. The negative values of excess intermolecular free length suggest that there exist strong interactions between the components of liquid mixture and positive values suggest weak interactions between the components of liquid mixture¹¹.

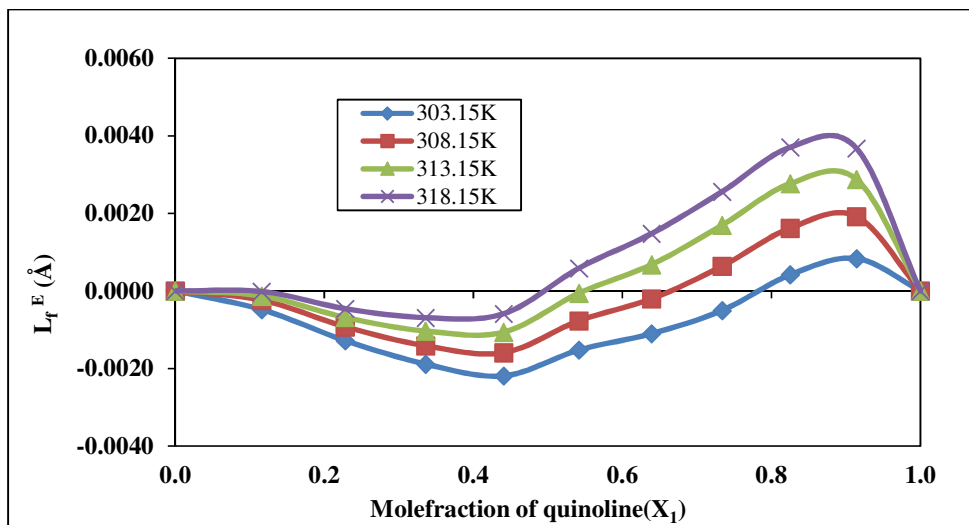


Fig-1: The variations of excess intermolecular free length (L_r^E) in binary liquid mixtures of (quinoline + mesitylene) with the mole fractions of quinoline at temperatures $T = (303.15, 308.15, 313.15$ and $318.15)$ K.

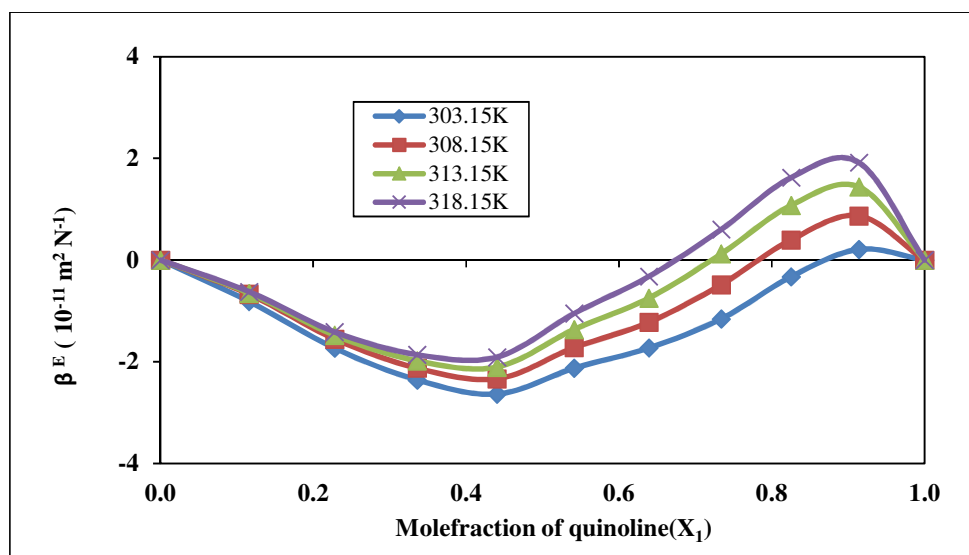


Fig-2: The variations of excess adiabatic compressibility (β^E) in binary liquid mixture of (quinoline + mesitylene) with the mole fractions of quinoline at temperatures $T = (303.15, 308.15, 313.15$ and $318.15)$ K.

These types of variations are also supported by Kerr effect. Fig-2 represents the variations of excess adiabatic compressibility (β^E) in binary liquid mixtures of (quinoline with mesitylene) over the entire mole fraction range of quinoline at temperatures $T = (303.15, 308.15, 313.15$ and $318.15)$ K. From Fig-2, it is observed that the variations of excess adiabatic compressibility (β^E) values are negative and positive in present the binary liquid mixtures. According to Fort and Moore¹², negative excess compressibility is an indication of strong heteromolecular interaction in the liquid mixtures which is attributable to charge transfer, dipole-dipole, dipole-induced dipole interactions, and hydrogen bonding between unlike components, while a positive sign indicates weak interaction and is attributed to dispersion forces (London forces), which are likely to be operative in every cases. In the present study, variations of excess compressibility are negative & positive in the present binary liquid mixture. This

observation together with Fort and Moore's result suggests the existence of strong intermolecular interactions up to 0.6 mole fraction range of quinoline and existence of weak interactions as the mole fraction of quinoline increases above 0.6. Fig-3 represents the variations of excess free volume (V_f^E) with the mole fractions of quinoline in the present binary liquid mixtures. It is observed from Fig-3 is that, V_f^E values are negative over the entire mole fraction range of quinoline. This suggests that the component molecules are more close together in the liquid mixture than in pure liquids forming the mixture, indicating that strong attractive interactions¹³ between component molecules such as hydrogen bonding, dipole-dipole interactions and other specific interactions between unlike molecules are operative in the system. The variations of excess enthalpy in the present binary system is shown in Fig-4. From Fig-4 it is observed that, H^E values are positive in the present binary system over the entire mole fraction range of quinoline. The positive values of H^E suggest strong interactions¹⁴ between the component molecules of liquid mixture.

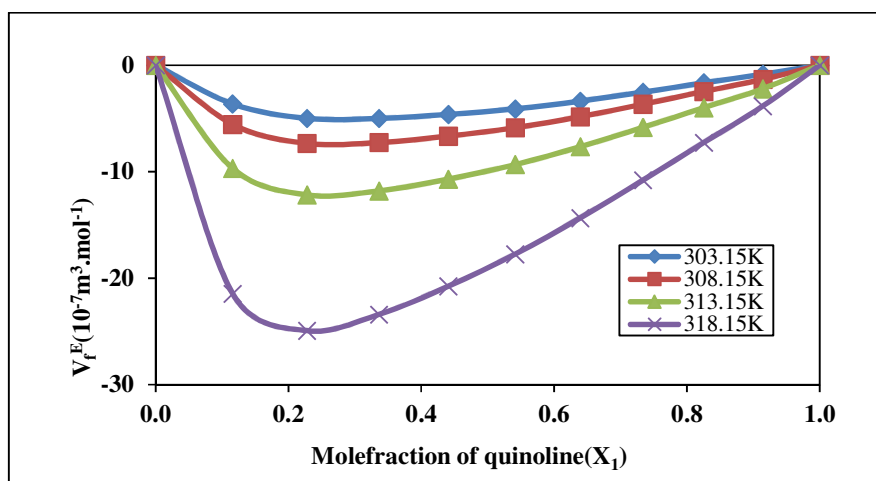


Fig-3: The variations of excess free volume (V_f^E) in binary liquid mixture of (quinoline+mesitylene) with the mole fractions of quinoline at temperatures $T = (303.15, 308.15, 313.15$ and $318.15)$ K.

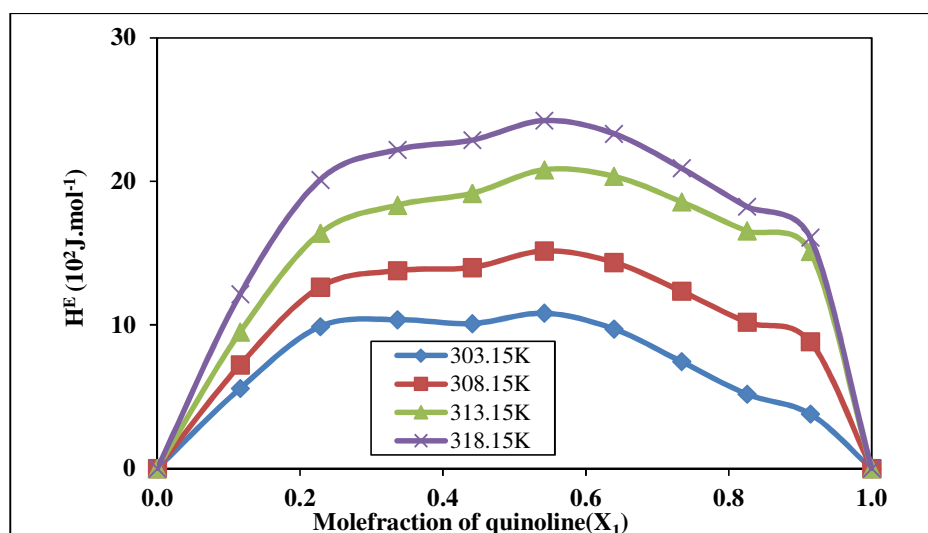


Fig-4: The variations of excess enthalpy (H^E) in binary liquid mixture of (quinoline+mesitylene) with the mole fractions of quinoline at temperatures $T = (303.15, 308.15, 313.15$ and $318.15)$ K.

CONCLUSIONS

Ultrasonic velocity, density and viscosity values are measured in the binary liquid mixtures containing quinoline with mesitylene at temperatures $T = (303.15, 308.15, 313.15 \text{ and } 318.15) \text{ K}$. By using these values, the excess thermodynamical parameters such as excess intermolecular free length (L_f^E), excess adiabatic compressibility (β^E), excess free volume (V_f^E) and excess enthalpy (H^E) are calculated over the entire mole fraction range of quinoline. An analysis of these results suggests the presence of strong intermolecular interactions^{15,16} in the present binary liquid mixtures. Also the strength of intermolecular interactions is observed to be decreased in the present binary system with temperature.

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