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Excess Properties Of Quinoline + Methanol + M-Xylene At Different Temperatures.

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ABSTRACT

Speed of sound, density and viscosity have been measured in pure Quinoline, m-xylene and methanol and in their ternary liquid mixtures with methanol as common component 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, β , free volume, V_f , intermolecular free length, L_f , and internal pressure, π , and their excess values have been calculated. 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 in terms of intermolecular interactions present in these mixtures.

Keywords: m-xylene, quinoline, speed of sound, viscosity, density

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INTRODUCTION

In predicting physico – chemical properties of liquid mixtures the measurement of speed of sound in pure liquids and liquid mixtures is found to be important. Thermodynamic and transport properties have been used to understand different kinds of association like molecular packing, molecular motion and various types of intermolecular interactions [1-5]. The liquids used in the present study are important due to their various industrial applications. Quinoline is used in solar cells to increase its efficiency and in dyes [6]. m- xylene is used as a co-polymer to alter the properties of polyethylene terephthalate (PET) making PET more suitable for the manufacture of soft drinking bottles [7]. Alcohols are self – associated organic liquids and are used as basic organic compounds for the synthesis of other organic compounds. The systematic investigation of excess properties are therefore of great importance. The present investigation is a study of effect of temperature variation on speed of sound, density, viscosity, excess adiabatic compressibility, β^E , excess free volume, V_f^E , excess intermolecular free length, L_f^E , and excess internal pressure, π^E , in quinoline + methanol+ m-xylene.

MATERIALS AND METHODS

The mass fraction of quinoline, methanol and m-xylene obtained from SDFCL are 0.98, 0.99 and 0.99 respectively. By using standard procedure [8,9] all the liquids were further purified. A good agreement was observed between experimental values of density, viscosity and speed of sound and the values reported in literature.

To prepare the mixtures in the required proportions Job's method of continuous variation was used. The mixtures were preserved in well – stoppered conical flasks. After mixing the liquids thoroughly the flasks were left undisturbed to allow them to attain thermal equilibrium. An electronic balance (Shimadzu AU Y220 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 in case of 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 were used in all calculations. The values are accurate to $\pm 10^{-3}$ mPa.s. A single crystal ultrasonic pulse echo interferometer (Model: F-80X, Mittal enterprises, India) was used for measuring speed of sound and were made at a fixed frequency of 3 MHz. The equipment was calibrated by measuring the velocity in carbon tetrachloride and benzene. 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.

Various parameters were evaluated using the standard equations [10]. The strength of interaction between the component molecules of the ternary mixtures is well reflected in the deviation of the excess functions from ideality. The excess properties such as β^E , V_f^E , L_f^E and π^E have been calculated using the equation

$$Y^E = Y_{\text{mix}} - [X_1Y_1 + X_2Y_2 + X_3Y_3] \quad (1)$$

where Y^E is β^E , V_f^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 speed of sound (u), density (ρ) and viscosity (η) values of ternary mixtures at 303.15, 308.15, 313.15 and 318.15 K are given in Table 1. Acoustical parameters namely adiabatic compressibility (β), free volume (V_f), free length (L_f) and internal pressure (π) have been calculated by using the experimental values of speed of sound, density and viscosity and are presented in Table 2.

Table 1: Speed of sound, density and viscosity of ternary liquid mixtures at different temperatures.

x_1	x_3	u (ms^{-1})	$\rho \times 10^{-3}$ (kg m^{-3})	$\eta \times 10^{-3}$ (NSm^{-2})	u (ms^{-1})	$\rho \times 10^{-3}$ (kg m^{-3})	$\eta \times 10^{-3}$ (NSm^{-2})
303.15 K				308.15 K			
0.0867	0.6603	1293.26	927.89	0.6943	1265.15	917.01	0.6061
0.1726	0.5754	1320.84	952.85	0.8369	1294.10	941.14	0.7413
0.2578	0.4912	1348.42	975.78	0.9909	1325.47	963.93	0.9078
0.3424	0.4076	1375.54	996.71	1.1738	1356.73	984.80	1.0735
0.4263	0.3248	1402.43	1015.60	1.3688	1388.78	1003.85	1.2716
0.5094	0.2426	1430.42	1033.79	1.6016	1421.31	1022.51	1.5088
0.5920	0.1611	1458.78	1051.20	1.8635	1453.05	1040.56	1.7635
0.6738	0.0802	1489.00	1067.12	2.1630	1486.42	1056.44	2.0492
313.15 K				318.15 K			
0.0867	0.6603	1243.89	911.47	0.5211	1222.05	904.61	0.3961
0.1726	0.5754	1272.63	934.77	0.6477	1250.94	927.92	0.5022
0.2578	0.4912	1304.31	956.96	0.7906	1282.00	949.78	0.6481
0.3424	0.4076	1338.31	978.33	0.9411	1315.21	970.66	0.7917
0.4263	0.3248	1370.89	997.94	1.1434	1349.73	990.84	0.9709
0.5094	0.2426	1405.89	1015.99	1.3368	1384.21	1009.77	1.2087
0.5920	0.1611	1440.00	1033.44	1.5945	1420.47	1027.92	1.4587
0.6738	0.0802	1474.73	1050.61	1.8512	1459.47	1045.17	1.7168

Table 2: Adiabatic compressibility (β), free volume (V_f), free length (L_f) and internal pressure (π) of ternary liquid mixtures at different temperatures.

x_1	x_3	β ($\times 10^{-11} \text{m}^2 \text{N}^{-1}$)				V_f ($\text{m}^3 \text{mol}^{-1}$)			
		303.15	308.15	313.15	318.15	303.15	308.15	313.15	318.15
0.0867	0.6603	64.4364	68.1304	70.9080	74.0217	767.49	910.55	1113.47	1635.83
0.1726	0.5754	60.1555	63.4466	66.0525	68.8680	619.36	720.42	860.28	1228.00
0.2578	0.4912	56.3633	59.0495	61.4252	64.0624	512.47	569.55	684.16	898.07
0.3424	0.4076	53.0254	55.1650	57.0694	59.5581	422.88	473.65	565.32	713.83
0.4263	0.3248	50.0629	51.6494	53.3202	55.3989	356.65	392.54	451.50	563.68
0.5094	0.2426	47.2759	48.4123	49.7975	51.6862	299.18	324.08	382.28	434.41
0.5920	0.1611	44.7028	45.5168	46.6649	48.2144	252.84	273.02	313.30	350.81
0.6738	0.0802	42.2666	42.8421	43.7657	44.9183	214.56	232.08	267.11	294.45
		L_f (m)				π (Nm^{-2})			
0.0867	0.6603	0.01592	0.01648	0.01694	0.01743	1215.97	1139.63	1061.41	928.99
0.1726	0.5754	0.01538	0.01591	0.01635	0.01681	1309.41	1234.86	1158.69	1024.04
0.2578	0.4912	0.01489	0.01535	0.01576	0.01621	1396.40	1337.16	1251.82	1137.56
0.3424	0.4076	0.01444	0.01483	0.01519	0.01563	1488.63	1421.97	1334.66	1228.36
0.4263	0.3248	0.01403	0.01435	0.01469	0.01508	1573.51	1512.23	1437.64	1328.80
0.5094	0.2426	0.01363	0.01389	0.01419	0.01456	1665.73	1610.11	1517.38	1448.13
0.5920	0.1611	0.01326	0.01347	0.01374	0.01406	1758.43	1702.39	1618.64	1553.22
0.6738	0.0802	0.01289	0.01307	0.01331	0.01357	1852.32	1792.44	1704.07	1643.91

The values of u , ρ and η are observed (from Table 1) to be increased with increase in mole fraction of quinoline. The decrease in values of adiabatic compressibility, β was observed with increasing concentration of quinolone, as observed from Table 2. It is primarily the compressibility that changes with structure which leads to change in speed of sound. The change in adiabatic compressibility in liquid mixtures indicates that there is a definite contraction on mixing and the variation may be due to complex formation. This clearly shows that there is a significant interaction between the three molecules.

A similar behaviour was observed for the intermolecular free length. L_f is a predominant factor in determining the variation of speed of sound in the mixtures. The decrease in the values of adiabatic compressibility and the free length with increase in speed of sound further supports the stronger molecular association [11] between unlike molecules. From Table 2, decrease in values of free volume and increase in values of internal pressure were observed. Further, the results clearly show the increasing magnitude of interactions [12].

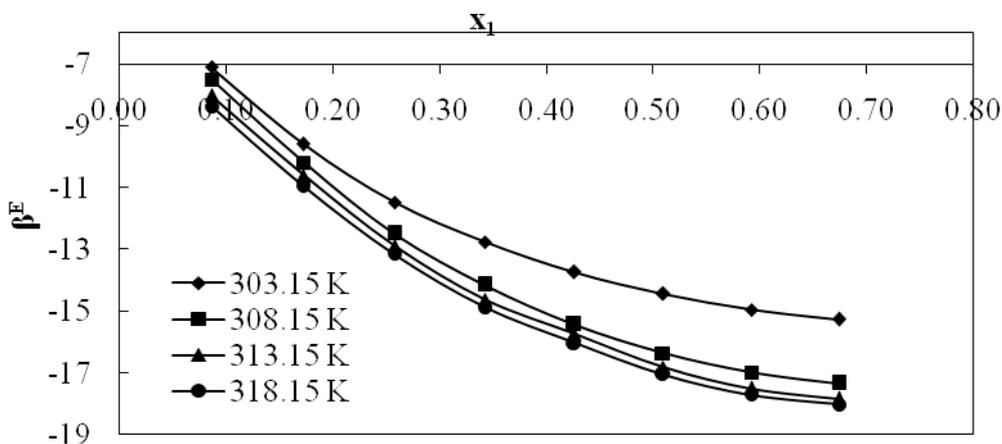


Fig 1: Variation of excess adiabatic compressibility (β^E) with mole fraction for quinoline + methanol + m-xylene system at different temperatures

From Fig.1 it is observed that β^E values are negative at all temperatures. The negative values indicate that the attractive forces between the molecules of components are stronger than the intramolecular attractions in each component. As the mole fraction of quinoline increases β^E values attain a more negative value. These observations support that they have a tendency for closer packing and hence are in a decreased compressibility phase in the intermolecular composition range and also observed that the molecular interaction are stronger. The magnitude of the contributions made by different types of interactions will vary with the components and composition of the mixture.

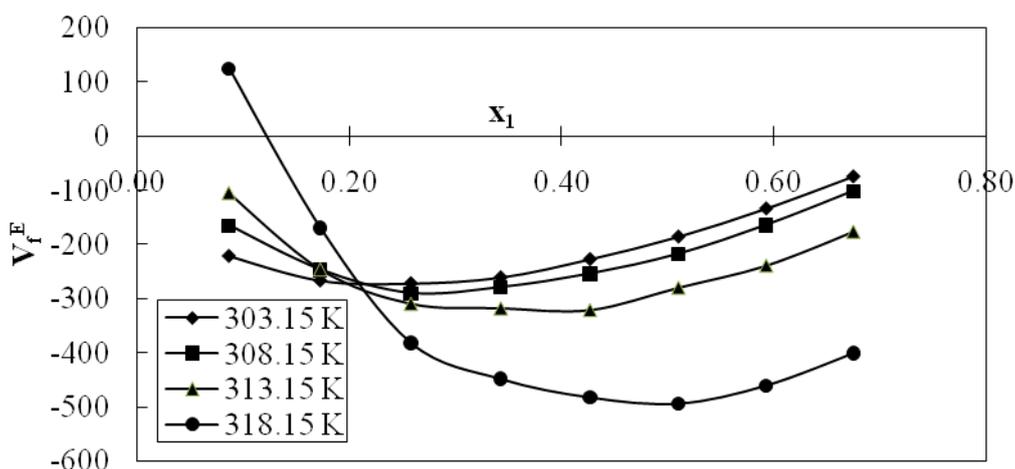


Fig 2: Variation of excess free volume (V_f^E) with mole fraction for quinoline + methanol + m-xylene system at different temperatures

From Fig.2 the values of V_f^E are observed to be negative. These values are observed to be less negative with increase of mole fraction. Increase in V_f^E values with increase in temperature is also observed from the same figure.

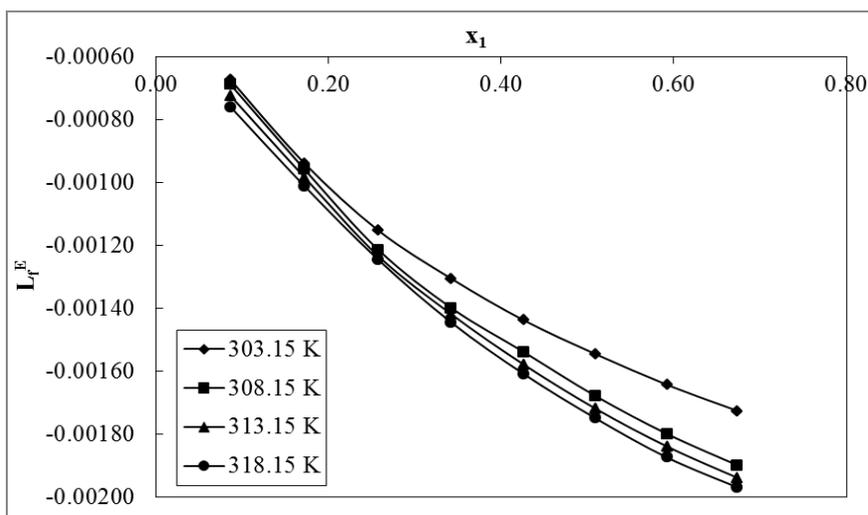


Fig 3: Variation of excess free length (L_f^E) with mole fraction for quinoline + methanol + m-xylene system at different temperatures

The excess free length values (Fig. 3) are observed to be negative at all temperatures. The negative L_f^E indicates that the sound wave needs to cover a large distance and it may be attributed to strong interactions between unlike molecules. It is observed that the values are more negative at higher temperatures and at higher mole fractions.

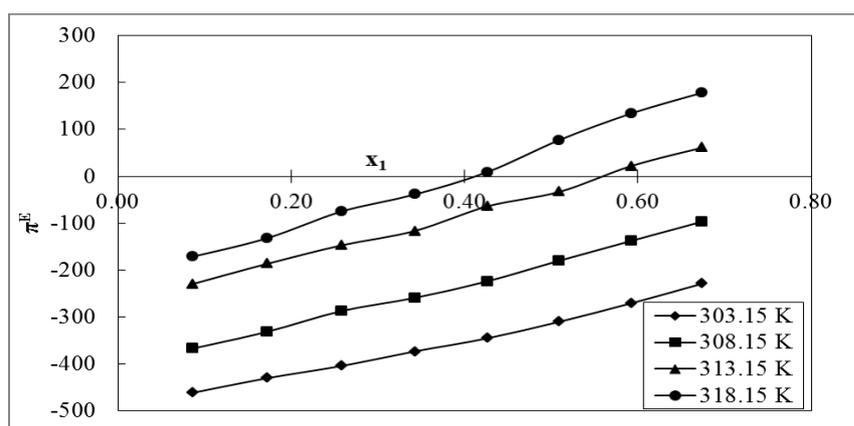


Fig 4: Variation of excess Internal Pressure (π^E) with mole fraction for quinoline + methanol + m-xylene system at different temperatures

The internal pressure is an interesting and valuable quantity that describes the macroscopic result of molecular interactions. The values of excess internal pressure for the systems at four different temperatures are represented graphically in Fig.4. π^E values are observed to be negative at lower mole fraction and positive at higher mole fraction. Increase in π^E values with increase in temperature was also observed from the same figure.

Extensive study of the excess properties of multicomponent systems reveals that the strength of interaction between two components is weakened by the addition of the third component. A good estimate of the extent of weakening of interaction has been discussed by Rastogi [13]. Thus, a ternary liquid system appears to be a typical example of the extent of weakening of interaction proportional to the number of components. The negative values of excess internal pressure support the presence of interactions between the molecules of the mixtures taken up for the study.

CONCLUSIONS

In this work, the experimental determination of speed of sound, density and viscosity data for the ternary system quinolone + methanol + m-xylene at 303.15, 308.15, 313.15 and 318.15 K was carried out. The excess parameters were calculated using the experimental values. β^E and L^E values are observed to be negative at all mole fractions. It is observed from the results that there exists strong molecular interaction between the unlike molecules.

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