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Density, Ultrasonic Velocity, Viscosity and their Excess Parameters of Some Binary Liquid Mixtures of Cumene with Aromatic Hydrocarbons at 298.15 K

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ABSTRACT

Density (ρ), viscosity (η) and sound velocity (u) of binary mixtures of ethyl benzene, toluene, mesitylene with cumene have been measured over the entire range of composition at temperature 298.15 K. From the experimental density, viscosity and sound velocity, the excess sound velocity (u^E) and deviation in viscosity ($\Delta\eta$) have been calculated. The excess sound velocity (u^E) is positive and deviations in viscosities are negative for all the binary systems studied over the whole composition. The results have been used to discuss the nature and strength of intermolecular interactions in these mixtures. The excess properties are found to be either negative or positive depending on the molecular interactions and the nature of the liquid mixtures.

Keywords: Density; Viscosity; Sound velocity; Cumene; Mesitylene; Viscosity deviation; Binary mixtures; Molecular interaction

INTRODUCTION

Densities, viscosities and sound velocity of solution are very important properties especially for the chemical design and for the optimization of chemical processes. The study of these properties plays an important role in many industrially interesting systems such as organic synthesis, ion extraction systems, gas adsorption solvents and mass transfer phenomena. Furthermore, the study of excess thermodynamics and transport properties for binary mixtures gives important information concerning the deeper understanding of the molecular liquid structure and intermolecular interactions [1]. Aromatic hydrocarbons are also important organic solvents in organic synthesis and extraction systems. Aromatic hydrocarbons like ethyl benzene, toluene, mesitylene were frequently used as octane enhancer in vehicles [2].

The excess molar volume and viscosity deviations are properties sensitive to different kinds of association in the pure components and in the mixtures. These properties have been used to investigate the molecular packing, molecular motions and various types of intermolecular interactions and their strengths, but these properties are influenced by the size, shape and chemical nature of the component molecules [3-5]. In view of this significance, it was thought worthwhile to study the binary mixtures of cumene with ethyl benzene, toluene, mesitylene in order to understand the interactions between these components. The lack of information has motivated us to undertake the present investigations.

MATERIALS AND METHODS

Chemicals/Materials

The chemicals used in the present work were high purity laboratory reagent grade samples of cumene, ethyl benzene, toluene, mesitylene were supplied by CDH Ltd. New Delhi, India with purity 99.5%. All chemicals was stored over sodium hydroxide pellets for several days and fractionally distilled twice. All the chemicals were stored in dark bottles over freshly activated molecular sieve to minimize adsorption of moisture. The purity of the solvent was ascertained by comparing the measured density, dynamic viscosities and sound velocity of the pure component at 298.15K with the available literature [6-10] as shown in Table 1. The reported experimental values of density (ρ), viscosity (η) and sound velocity conform closely to their corresponding literature values, with an average of the absolute value of deviation $3.6 \times 10^{-3} \text{ kg m}^{-3}$ and $3.3 \times 10^{-3} \text{ m. Pa. s.}$

Table 1: Experimental properties of pure liquid at 298.15 K.

Name of Liquid	Density		Viscosity		Sound Velocity	
	Obs.	Lit.	Obs.	Lit.	Obs.	Lit.
Cumene	0.8532	0.8581 [6]	0.7337	0.7388 [6]	1326	1325 [6]
Toluene	0.8672	0.8621 [7]	0.5691	0.5525 [9]	1312	13.05 [7]
Ethyl benzene	0.863	0.8625 [7]	0.6345	0.628 [8]	1308	13.05 [7]
Mesityline	0.8616	0.8612 [7]	0.6049	0.667 [10]	1338	1336 [7]

Apparatus and procedure

Air tight stopper bottles were used for the preparation of the mixtures and were placed in the dark place. The losses in the mixtures were kept to minimum, as evidenced by repeated measurements of physical properties over an interval of 2-3 days during in which before use time no change in physical properties was observed. The mixtures were well mixed by shaking before use. Binary mixtures were prepared by mass, using an electronic analytical balance (Model K-15 Deluxe, K Roy Instruments Pvt. Ltd.) with an accuracy of $\pm 0.00001 \times 10^{-3}$ kg as described elsewhere. The possible error in the mole fraction was estimated to be less than 1×10^{-4} . Five samples were prepared for one system and their density and sound velocity were measured on the same day.

Density: Densities of pure liquids and their binary mixtures were determined by using a R. D. Bottle with a 25 cm^3 is used to measure the densities (ρ) of pure liquids and binary mixtures. The R. D. Bottle is calibrated by using conductivity water (having specific conductance less than $1 \times 10^6 \text{ ohm}^{-1}$) with 0.9970 and 0.9940 gcm^{-3} as its densities at $T=298.15 \text{ K}$, respectively. The R. D. Bottle filled with air bubbles free liquids is kept in a thermostate water bath (MSI Goyal Scientific, Meerut, India) controlled with a thermal equilibrium. The precision of the density measurements was estimated to be $\pm 0.0002 \text{ g cm}^{-3}$.

Sound velocity: The ultrasonic velocities were measured using a multi-frequency ultrasonic interferometer (Model F-80D, Mittal Enterprise, New Delhi, India) working at 3 MHz. The meter was calibrated with water and benzene at 298.15 K. The measured values of ultrasonic velocities of pure cumene, ethyl benzene, toluene and mesitylene at 298.15 K were 1326, 1308, 1312 and 1338 m.s^{-1} respectively, which compare well with the corresponding literature values

Viscosity: The viscosity of pure liquids and their binary mixture were measured using suspended Ostwald viscometer having a capacity of about 15 ml and the capillary having a length of about 90 mm and 0.5 mm internal diameter has been used to measure the flow time of pure liquids and liquid mixtures and it was calibrated with triply distilled water, methanol and benzene at 298.15 K. The details of the methods and techniques have been described by researchers. The efflux time was measured with an electronic stop watch (Racer) with a time resolution (± 0.015) and an average of at least four flow time readings was taken. Glass stopper was placed at the opening of the viscometer to prevent the loss due to evaporation during measurements. The two bulbs reservoir, one at the top and other at the bottom of the viscometer linked to each other by U type facilitate the free full of liquid at atmospheric pressure.

Theoretical: The excess sound velocity (u^E) is evaluated from the experimental values of ultrasound velocities for component liquid and their binary mixtures by:

$$u^E = u_{1,2} - u_1 X_1 + u_2 X_2 \quad (1)$$

Where $u_{1,2}$ is ultrasound velocity in the mixture and u_1, u_2, X_1, X_2 are the sound velocities and mole fractions respectively of the component liquid 1 and 2. The ultrasonic velocity (u), density (ρ) and viscosity (η) in pure liquids and liquid mixtures of various concentrations have been measured at 298.15 K.

Viscosity deviations: The viscosity deviations ($\Delta\eta$) with mole fraction were calculated by the following:

$$\Delta\eta (\text{m} \cdot \text{Pa} \cdot \text{s}) = \eta_{12} - \sum_{i=1}^2 x_i \eta_i \quad (2)$$

Where, x_i, η_i and η_{12} refer, respectively, to the mole fraction and viscosities of i^{th} pure components and of the binary mixtures. The excess value of A^E of these thermodynamic parameters have been obtained by subtracting the ideal value from the experimental value:

$$A^E = A_{exp} - (X_1 A_1 + X_2 A_2)$$

Where A represents the parameter such as intermolecular free length, molar volume, available volume, free volume and isentropic compressibility and X_1 and X_2 are the mole fractions of components whose parameters.

RESULT AND DISCUSSION

The experimental values of densities and viscosities of the hydrocarbons are compared with the literature values and are presented in Table 2. It was found that the experimental values are in proximity with the literature values. Insufficient data on densities, viscosities and sound velocity of pure cumene, ethyl benzene, toluene, mesitylene is available. The densities, ρ , viscosities, η and sound velocity, u , of binary mixtures were measured at 298.15 ± 0.01 K as a function of the composition of the corresponding binary mixtures. The results of the study are presented in Table 3.

Table 2: Experimental results for the binary liquid mixtures at 298.15 K.

Mole fraction (x_1)	Density (ρ) g.cm ⁻³	Sound velocity (u) m.s ⁻¹	Viscosity (η) mPa.s
Cumene+ethyl benzene			
0	0.863	0.6345	1308
0.1193	0.8612	0.6472	1310
0.2209	0.8602	0.6633	1314
0.3312	0.8596	0.6715	1316
0.4397	0.8592	0.3882	1317
0.5319	0.8588	0.6931	1318
0.6395	0.858	0.7042	1320
0.7301	0.8572	0.7124	1321
0.8315	0.8564	0.7198	1322
0.9313	0.8554	0.7249	1324
1	0.8532	0.7337	1326
Cumene+toluene			
0	0.8672	0.5691	1312
0.1193	0.8628	0.5801	1314
0.2209	0.8612	0.6046	1315
0.3312	0.86	0.6293	1316
0.4397	0.8592	0.6457	1318
0.5319	0.8584	0.6706	1390
0.6395	0.8576	0.6869	1320
0.7301	0.8568	0.7032	1321
0.8315	0.8556	0.7191	1322
0.9313	0.8544	0.7266	1324
1	0.8532	0.7337	1326
Cumene+mestyline			
0	0.8616	0.6049	1338
0.1193	0.8612	0.6216	1336
0.2209	0.8608	0.6384	1335
0.3312	0.8604	0.6551	1334
0.4397	0.8601	0.6718	1333
0.5319	0.8596	0.6885	1332
0.6395	0.8592	0.6967	1331
0.7301	0.8588	0.7048	1330
0.8315	0.8584	0.713	1329
0.9313	0.8576	0.7293	1328
1	0.8532	0.7337	1326

Table 3: Excess properties for the binary liquid mixtures at 298.15 K.

Mole fraction (x_1)	Excess sound velocity (u^E) ms^{-1}	Excess viscosity (η^E) $\text{mPa}\cdot\text{s}$
Cumene+ethyl benzene		
0	0	0
0.1024	0.805448391	0.003592714
0.2117	1.316815648	0.005614672
0.3214	1.68579313	0.006837461
0.4617	1.862323267	0.007159198
0.5001	1.869044887	0.006826376
0.6616	1.712750618	0.005826448
0.7088	1.445886092	0.00454673
0.8079	1.00261098	0.002721492
0.9026	0.419256162	0.000601783
1	0	0
Cumene+toluene		
0	0	0
0.1024	0.352395	0.002101
0.2117	0.481198	0.003442
0.3214	0.574776	0.00443
0.4617	0.619846	0.004927
0.5001	0.621524	0.00498
0.6616	0.580937	0.004611
0.7088	0.511226	0.003941
0.8079	0.394676	0.002802
0.9026	0.240228	0.00128
1	0	0
Cumene+mesitylene		
0	0	0
0.1024	0.404023349	0.003795502
0.2117	0.737973565	0.006802694
0.3214	1.041263206	0.008969213
0.4617	1.251599686	0.010007761
0.5001	1.340694954	0.010055889
0.6616	1.316287178	0.009162538
0.7088	1.169430526	0.007632876
0.8079	0.846797677	0.005095458
0.9026	0.344591461	0.00176434
1	0	0

The values of $\Delta\eta$ are negative for all the selected binary mixtures and regularly decrease with an increase in $-\text{CH}_3$ groups from benzene to mesitylene. The deviations in viscosity of binary mixtures are essentially due to two factors (in general).

- The depolymerization of the associated entities like hydrocarbons and formation of monomeric moieties on mixing make a negative contribution to $\Delta\eta$ values.
- Replacement of like contents in pure components by unlike contents in mixture makes positive contributions to $\Delta\eta$ values.

Negative values of $\Delta\eta$ throughout the whole composition range and at all temperatures suggest that the intermolecular interaction becomes weaker on mixing of components, also indicating that the dispersion type of forces is predominant in these mixtures. The negative $\Delta\eta$ values support the positive u^E values and account for dispersive forces in these binaries. $\Delta\eta$ values are also expected to be negative because of vast different in

viscosities of pure components (Table 2). The negative values of $\Delta\eta$ at equimolar concentrations of 1-iodobutane and hydrocarbons mixtures are in the following order: Benzene>toluene>ethyl benzene>mesitylene.

The deviation in ultrasonic velocity with the mole fraction of cumene for the three systems indicates that there is a non-linear decrease in velocity without having any minimum as shown in Figure 1. The non-existence of maxima or dip at any intermediate concentration of cumenet with ethyl benzene, toluene and mesityline indicate that there is no complex formation between components. These observations are in agreement with the general trends of the ultrasonic velocity variations in binary liquids. The existence of structure differences in species in solution is bound to have its effect in the other physical parameters.

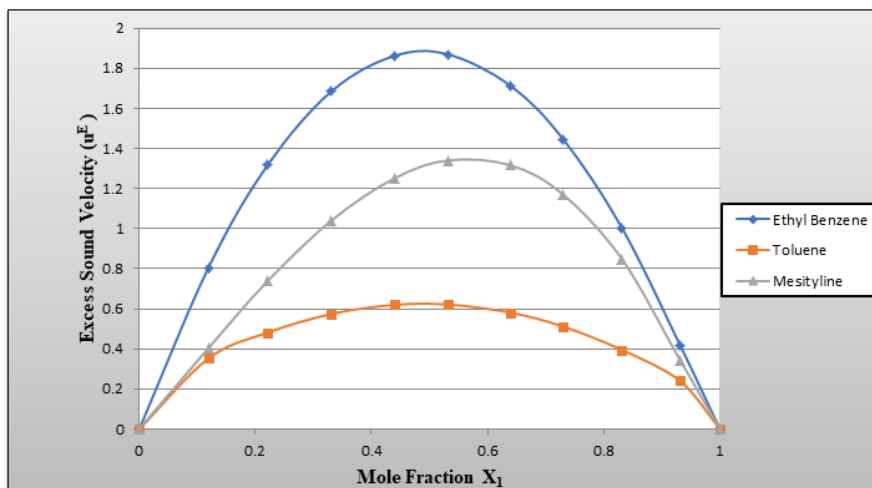


Figure 1: Variation of deviation in sound velocity with mole fraction.

The diversity in viscosity ($\Delta\eta$) gives a quantitative estimate of intermolecular interactions. The $\Delta\eta$ at each composition is obtained from the relation suggested by Fort and Moore. The diversity in viscosity becomes positive as the strength of interaction increases. The $\Delta\eta$ values may be generally explained considering on the following factors:

- The differences in the size and shape of the component molecules and the loss in dipolar interactions in pure components may contribute to a decrease in viscosity.
- The specific interactions between unlike molecules in hydrogen bond formation and charge transfer complex may lead to increase in viscosity in combinations than in pure components.

The later effect introduces positive deviation while the former effect produces negative deviation in viscosity. The net deviation in viscosity is generally considered as a result of the two major effects. The deviations in viscosity for the three systems at the temperature (298.15 K) are negative indicating the dominance of nonspecific interactions between unlike molecules.

The experimental values of viscosities as a function of mole fraction of trichloroethylene for three systems are shown in Figure 2. The three systems exhibit a positive deviation of excess viscosity over entire mole fraction range with a maximum corresponding to a mole fraction of about 0.5 at the temperature studied. These deviations indicate specific molecular interactions between different molecules.

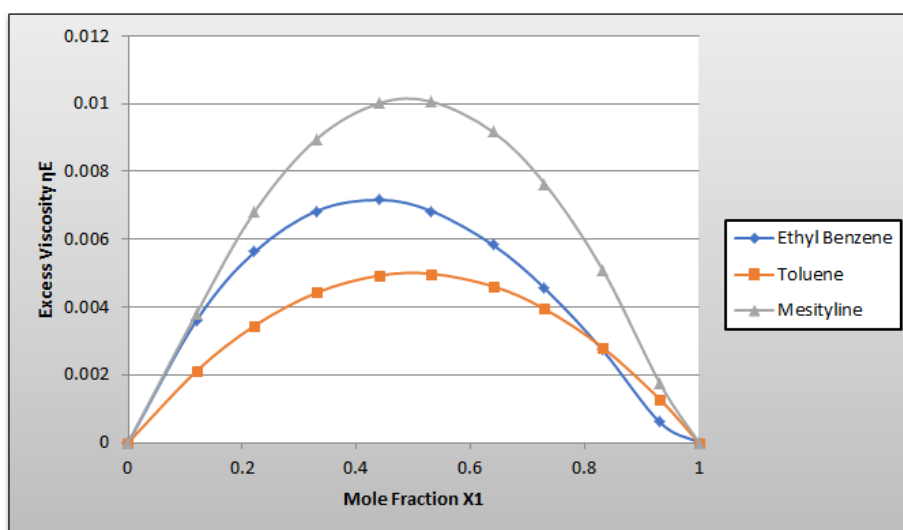


Figure 2: Variation of deviation in viscosity with mole fraction.

CONCLUSION

The excess sound velocity, u^E and deviations in viscosity, $\Delta\eta$, have been calculated from the experimental values at 298.15K for cumene, ethyl benzene, toluene, mesitylene binary mixtures. the sign and magnitude of these quantities have been discussed in terms of the molecular interactions

between the mixing components. The deviation in viscosity and sound velocity show positive behavior, for the systems under investigation indicating strong interactions between the components. However, the deviation in sound showed positive trend.

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DECLARATIONS CONFLICT OF INTEREST

The authors have no competing interests to declare that are relevant to the content of this article.

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DATA AVAILABILITY STATEMENT

All data generated or analyzed during this study are included in this published article.

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