Volumetric and Ultrasonic study of molecular interaction in binary liquid mixtures over the temperature range (303-318) K

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Abstract: The experimental data of densities (ρ) and ultrasonic velocities (U) of binary mixtures of (Nitrobenzene + Benzene) and (N, N-Dimethyl formamide + Benzene) over the entire composition range at four different temperatures T = (298, 308, 313 & 318.15) K and at one atmospheric pressure have been reported. The obtained data’s are used to compute adiabatic compressibility (β), Intermolecular free length (Lf), acoustic impedance (Z), molar volume (Vm), molar sound velocity (R), molar compressibility (W), Relative association (RA), excess volume (VE) and Excess adiabatic compressibility (βE). The results obtained in this study have been interpreted in terms of the existence of dipole-dipole and dipole induced intermolecular interactions between the compounds in the liquid mixture under study.

Keywords: Density; Ultrasonic velocity; liquid mixture; intermolecular interactions.

I. Introduction

Recent development in science have found profound applications of liquid mixtures in the field of medicine, engineering, agriculture and other industrial applications, the study and understanding of thermodynamic and transport properties are more essential [1, 2]. Measurement of density and ultrasonic velocity has been adequately employed in understanding the molecular interactions in pure, binary, and higher order multi component liquid mixtures [3, 4]. The propagation of ultrasonic velocity in a medium is a thermodynamic property and has come to be recognized as a very specific and unique tool for predicting and estimating various physico-chemical properties of the liquid mixtures under consideration [5-7]. In recent years, there has been considerable interest in theoretical and experimental investigations of the excess thermodynamic properties of binary mixtures. In principle, the interaction between the molecules can be established from the study of the characteristic departure from ideal behaviour of some physical properties (i.e., volume, compressibility, and viscosity). The excess thermodynamic functions are sensitive to the intermolecular forces as well as to the size of the molecules. In order to study all these molecular-kinetic properties of liquids and liquid mixtures, low amplitude ultrasonic wave is very valuable. Ultrasonic methods have established a permanent place in science and new applications and found for the solution of many theoretical and practical problems. Most important features of ultrasonic systems are robustness, non-invasiveness, precision, low cost, rapidity and easy automation. Sometimes it becomes difficult to do thermo-acoustical study with actual liquid mixture system, in such cases mixtures of models compounds, often called surrogate mixtures, are useful for building an understanding of the physical properties and chemical reactions of complex fuel mixtures. Surrogate fuels can provide a baseline for engine performance, and they can help in making predictions for the more complex fuel [8-10]. A detailed survey of literature shows that very less work has been done for (Nitrobenzene + Benzene) and (N, N-Dimethyl formamide + Benzene) mixtures. Keeping all these important applications of thermodynamic and acoustic study in our mind, we have studied the said property for (Nitrobenzene + Benzene) and (N, N-Dimethyl formamide + Benzene) mixtures over the entire composition range at four different temperatures $T = (298, 308, 313 & 318.15)$ K and at one atmospheric pressure.
II. Experimental

The chemicals of analytical grade were purchased from Sigma-Aldrich (purity greater than 99%) and were used after drying over molecular sieves. The purity of chemicals was checked by comparing the measured densities and ultrasonic sound velocity, which are in good agreement with literature values [11, 12]. To minimize evaporation losses and light effects the mixtures were prepared by mixing the measured volumes of the components in airtight brown bottles. Density measurements were made with a (single pan) mettler balance. The temperature of the test liquids and binary mixtures was maintained to an accuracy of ±0.1 K in an electronically controlled thermostatic water bath. Ultrasonic velocities were determined by using multi frequency ultrasonic interferometer (F81, Mittal Enterprises) which obtains the speed of sound by using a crystal controlled variable path ultrasonic interferometer operating at a frequency of 1 MHz. The temperature stability is maintained ±0.1 K by circulating thermostated water around the cell with a circulating pump. In all, the accuracy of the determined value of densities and ultrasonic velocities work out to be ±0.0001 gm/cm³, and ±0.2 m/s respectively.

III. Results and Discussion

Densities (ρ) and Ultrasonic velocities (U) of binary mixtures of (Nitrobenzene + Benzene) and (N, N-Dimethyl formamide + Benzene) have been measured at 303 K, 308 K, 313 K and 318 K over the entire range of volumes fraction. Various acoustical parameters were calculated from the measured values of densities and ultrasonic velocity by using the following relations [13-15].

Newton-Laplace equation is used to calculate adiabatic compressibility (β) = 1/[(U²/ρ)] .......... (1)

Intermolecular free length (Lₐ) = K(β)½ ......... (2)

Acoustic impedance (Z) = ρU ........... (3)

Molar volume (Vₘ) = x₁M₁ + x₂M₂ / ρ ........... (4)

Molar sound velocity (R) = U/³V ............ (5)

Molar compressibility (W) = M/ρβ⁻³/⁷ ........... (6)

Relative association (Rₐ) = (ρ₂/ρ₁)(u₁/u₂) ........... (7)

For ideal mixing ideal value of a parameter is given by Excess volumes Yideal = (1-x)Y₁ + xY₂ ........... (8)

Excess parameter is given by Yₑ = Yexp - Yideal ............ (9)

Where, M is the mean molecular weight; the subscripts 1 and 2 stand for pure solvent (benzene) and solutions of (Nitrobenzene + Benzene & N, N-Dimethyl formamide + Benzene) respectively. K representing a temperature-dependent constant [16]. T absolute temperature. The measured values of ultrasonic velocity, density and related thermo acoustical parameters of Nitrobenzene + Benzene and N, N-Dimethyl formamide + Benzene solutions at 303 K, 308 K, 313 K and 318 K temperatures in different concentrations are shown in Tables 1 and 2. The variation of different thermo acoustical parameters with concentrations and temperature is shown graphically in Figures 1-6. It can be seen from table 1 and 2 that the density of binary mixtures increases with the increase in concentration of solute in the solution and decreases slightly with increase in the temperature at a particular concentration. It is also evident from Table 1 and 2 that, ultrasonic velocities are increasing with the increase in concentration for both nitro benzene and N, N-Dimethyl formamide in benzene at all the studied temperatures. Generally, studies of thermo-acoustical and excess thermo-acoustical parameters [17, 18] are useful to explain strength of the interactions between the component molecules of liquid mixtures in most of the cases. Intermolecular free length is an important parameter that has association with adiabatic compressibility. The variation in Lₐ values for the binary mixtures at different temperatures shown in figure 1 and 2. It is clear that the intermolecular free length shows a similar behaviour as reflected by β from Table 1 and 2. The decreased compressibility brings the molecules to a closer packing resulting a decrease in intermolecular free length. The inter dependence of 'Lₐ' and 'U' has been evolved from a model for sound propagation proposed by Eyring and Kincaid [19]. According to the proposed theory, the decrease in the value of β' and 'Lₐ' with increase in ultrasonic velocity further strengthens the process of complex formation between the solute molecules through hydrogen bonding due to which structural arrangement is considerably altered. In the present study also, there is a possibility of complex formation due to interactions as revealed by the nonlinear variation of ultrasonic velocity and their related parameters due to strong interaction of forces.
Table 2: Ultrasonic velocity, density, adiabatic compressibility, intermolecular free length, acoustic impedance, Molar volume, excess adiabatic compressibility, excess volume, molar sound velocity, molar compressibility, Relative association for Nitrobenzene + Benzene at T= (303, 308,313 and 318) K.

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<th>$\rho$ (kg/m$^3$)</th>
<th>U (m/s)</th>
<th>$\beta \times 10^{-10}$ (N-m$^2$-kg$^{-1}$)</th>
<th>L$_x$ $\times 10^{11}$ (m)</th>
<th>Z $\times 10^{5}$ (kg-m$^{-2}$-s$^{-2}$)</th>
<th>V$_m$ $\times 10^{-6}$ (m$^3$-mol$^{-1}$)</th>
<th>$\beta^E \times 10^{12}$ (N-m$^{-3}$-mol$^{-1}$)</th>
<th>$V^E \times 10^{5}$ (mol-m$^{-3}$)</th>
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Table 3: Ultrasonic velocity, density, adiabatic compressibility, intermolecular free length, acoustic impedance, Molar volume, excess adiabatic compressibility, excess volume, molar sound velocity, molar compressibility, Relative association for N, N-Dimethyl formamide + Benzene at T= (303, 308,313 and 318) K.

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Figure 1: Intermolecular free length versus volume fraction for Nitro-benzene.

Figure 2: Intermolecular free length versus volume fraction for N, N-Dimethyl formamide.
This conclusion is further fortified by the increasing values of relative association $R_A$, because the increase of $R_A$ with the addition of co-solvent (table 1 and 2) suggests that the chemical force predominates over the breaking up of the solvent molecules [20]. The acoustic impedance ($Z$) is the parameter related to the elastic properties of the medium. Therefore, it is important to examine specific acoustic impedance in relation to concentration and temperature. Fig. 1 and 2 shows the variation of acoustic impedance with mole fraction and temperature. Acoustic impedance exhibits a nonlinear variation with concentration further supports the possibility of presence of strong interaction forces. Table 1 and 2 also refers that, the variation in molar sound velocity and molar compressibility with mole fraction shows similar trend interactions are increasing with increase in mole fraction of solute. The variation of excess volume and excess adiabatic compressibility with volume fraction in the binary mixtures are given in Fig. 3, 4 and Fig. 5, 6 respectively. According to Sri Devi et. al. [21], negative excess values are due to closely packed molecules which accounts for the existence of strong molecular interactions whereas positive excess values reflect weak interactions between unlike molecules. The sign of excess volume & excess adiabatic compressibility are useful in assessing the compaction due to molecular interactions in liquid mixtures through hydrogen bonding, charge transfer, dipole-dipole & dipole induced dipole interactions, interstitial accommodation and orientation ordering, which lead to a more compact structure, leading to negative values of the excess adiabatic compressibility and excess molar volume. It can be explained as, velocity of ultrasonic wave is a sensitive function of space filling factor, and small change in volume causes significant change in velocity of ultrasonic wave. The volume change of the liquid mixture depends upon the structural arrangement in the liquid mixture as well as on intermolecular interactions. The forces between the molecules and also their geometry would decide the structural arrangement. Thus, the geometry of molecules has a vital role in deciding the volume of a liquid. In a mixture of two liquids, the shape of molecules i.e. cluster geometry or micro geometry would therefore, predominantly, decide
an excess of molar volume. An increase in the strength of the heteromolecular forces manifesting in a decrease in adiabatic compressibility of the mixture would tend to reduce the size of cluster, hence decrease in total volume of the mixture. From table 2 and 3 it can be seen that the variation of $V^E$ and $\beta^E$ are negative and non-linear with at least one minimum. Such a variation with minimum at certain composition is known to indicate an attractive heteromolecular liquid-liquid interaction, leading to association of molecules and a cluster may be formed. Two minima can be considered to form two relatively stable clusters. The process leading to the stable clusters would be in equilibrium at these concentrations evident form figure 2 and 3. Let the pure liquids A and B be represented as: $A_{liq} = (A, A, A, A, A, A,...)$, and $B_{liq} = (B, B, B, B, B, B,...)$ i.e. a set of monomers, dimmers, trimmers, etc, due to an associative heteromolecular AB interaction, the mixture can be $(AB)_{liq} = (A, B, A, B, A, B,...)$ i.e. formation of clusters evidencing strong intermolecular interaction, leading to association of molecules and a cluster may be formed. Two minima can be considered to form two relatively stable clusters. The process leading to the stable clusters would be in equilibrium at these concentrations evident form figure 2 and 3. Let the pure liquids A and B be represented as: $A_{liq} = (A, A, A, A, A, A,...)$, and $B_{liq} = (B, B, B, B, B, B,...)$ i.e. a set of monomers, dimmers, trimmers, etc, due to an associative heteromolecular AB interaction, the mixture can be $(AB)_{liq} = (A, B, A, B, A, B,...)$ . This association would occur due to presence of an attractive subgroup in A type and attractive subgroup in B type molecules. If minima is closer to higher concentration of A then, $AA>BB$, while a symmetrical variation would indicate $AB>AA$ as well as $AB>BB$ as the relative strength of interactions. We can explain the observations of of $V^E$ and $\beta^E$ for nitrobenzene and benzene system which is a mixture of Polar-nonpolar molecules considering the above facts of molecular interaction. Excess volume & excess adiabatic compressibility both have negative for nitro-benzene + benzene system. The types of interaction are AA & BB as two deeps are observed in figure 3. The peak at $x=0.5$ in $V^E$ and minima in $\beta^E$ indicates the complex formation in these mixture at $x=0.5$. Association between A type to form $A, A, A, A, A, A,...$ as well as in B molecule of the type $B, B, B, B, B, B,...$ , i.e. formation of aggregates of pure component as well as stable clusters at equal composition may be the reason for decrease in volume and adiabatic compressibility and presence of dipole-induced dipole type intermolecular force [22]. The second mixture of N, N-Dimethyl formamide + Benzene falls in the same category of polar-nonpolar molecule. Figure 4 shows that excess volume varies with volume fraction smoothly and $V^E < 0$. N,N dimethyl formamide has a dipole moment 3.83D indicating a strong polar nature and benzene is neutral. In the mixtures of N, N dimethyl formamide-benzene the polar molecule may be inducing dipole causing attraction resulting in decrease in volume. The negative variation in $\beta^E$ support a strong interaction forces may be due to dipole-induced dipole and indicating formation of clusters. Both the type of molecules contributes equally to AB type of attractive interaction. From the figure 3, 4 and 5, 6 it is revealed that there is a strong interaction in both the mixtures, but the strength of interaction in nitrobenzene-benzene is more than in benzene-N,N dimethyl formamide at all temperatures. Nitrobenzene being strongly polar (4.22D) induces the dipole in the mixtures with benzene causing more strength of interaction in nitrobenzene + benzene system than N, N dimethyl formamide + benzene mixture [23].

IV. Conclusion

The nonlinear variation of the related parameters such as adiabatic compressibility, intermolecular free length, acoustic impedance were elaborated to understand the molecular interactions that leads to the process of complex formation between the solute molecules through dipole-dipole interactions. The negative values of the excess volume and excess adiabatic compressibility with concentration and temperature confirms the presence of strong solute-solvent interaction through dipole-induced dipole interactions. Overall prediction in these mixtures is interactions are due to dipole-induced dipole forces and extent is greater in nitrobenzene-benzene compared to N, N dimethyl formamide + benzene.

V. References