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Research Article

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Interactions study by free volume of Pyridine and Aniline

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ABSTRACT

Measurements of the ultrasonic velocity and density with the viscosity are very important to find out the different basic properties of the liquid and their mixtures. These properties can be studied with simplicity and accuracy by the ultrasonic technique, therefore more preferred than the other methods. Here the measurements of Ultrasonic velocity (υ) with density (ρ) and coefficient of viscosity (η) are carried out to find out the different ultrasonic parameters with varying composition of the binary system at three temperatures 303, 308 & 313K. The results have been discussed and graphically plotted. The determinations of excess values are so important that they provide details of the strength of the any existing interaction. Therefore the excess values of the above parameters are also evaluated and the results are shown graphically. The data confirms the existence of interaction in the binary mixture.

Keywords: velocity, compressibility, free length, internal pressure, molecular interaction

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INTRODUCTION

It is very important to study the intermolecular interactions in many branches and fields of advanced research. There are so many methods available for understanding the nature of intermolecular interaction and the different forces between the molecules but Ultrasonic studies have always played an important role in the study of liquids and liquid mixtures. The ultrasonic investigations of liquid mixtures are important in understanding the physical nature and strength of molecular interactions. The ultrasonic velocity of liquid is basically related to the bonding forces between the atoms and molecules. It helps to understand the nature of molecular interactions in pure and binary mixtures of the liquids[1-6]. There have many researchers studied previously the binary mixtures of the various compounds but a little attempt has been made to study the ultrasonic and thermodynamic properties of pyridine. The Pyridine is an important liquid used in the extraction processes for coal to analyze its compounds and in the manufacture of vitamin B_6 and other drugs. Similarly Aniline is also important in many applications such as bio-medical, chemical and pharmaceuticals. Therefore these liquids & their mixtures are of interest to organic chemists to know about the type of bond and number of molecule in the formation of complexes[7-8]. In order to understand the nature of molecular interactions between the components of the liquid mixtures, it is of important to discuss the different parameters in terms of their excess values rather than actual.

In the present study the ultrasonic velocity, density and viscosity measurements have been carried out for various concentrations and at three different temperatures 303, 308, and 313K. The variations of different ultrasonic parameters and their excess values with respect to concentration of aniline in the mixture at different temperatures are studied to understand molecular interactions.

EXPERIMENTAL SECTION

The chemicals Aniline and Pyridine were obtained commercially of AR grade with purity of 99.5% and used without further purification. Ultrasonic velocities (υ) for different concentrations of pure liquids and binary mixtures were measured using Ultrasonic Interferometer at 1 MHz (Mittal enterprises- model M-81). The density measurements were carried out by using specific gravity bottle. The viscosities were measured using suspended level viscometer. The experimentally measured density (ρ) in kgm^{-3}, ultrasonic velocity (υ) in ms^{-1} and viscosity (η) in Nsm^{-2} are used to evaluate various parameters by using the standard relations such as

Adiabatic Compressibility (β_α),

$$\beta_\alpha = \upsilon\ \rho \qquad \text{----------1,}$$

Intermolecular free length (L_f)

$$L_f = K\beta_\alpha^{\ 1/2} \qquad \text{----------2,}$$

Acoustical Impedance (Z)

$$Z = \rho\upsilon \qquad \text{----------3,}$$

Where, K –is temperature dependant constant 211.25 X 10^{-8} at 313.15 K and T – absolute temperature [9],

free volume (V_f),

$$V_f = \left[\frac{M_{eff}\,\upsilon}{\eta\kappa}\right]^{3/2} \qquad \text{---------- 4,}$$

Where M_{eff} is the effective molecular weight ($M_{eff}=\Sigma m_i X_i$), k is temperature independent constant which is equal to 4.28 X 10^9 for all liquids.
The internal pressure (π_i),

$$\pi_i = bRT\left[\frac{\eta\kappa}{\upsilon}\right]^{1/2}\left[\frac{\rho^{2/3}}{M_{eff}^{\ 7/6}}\right] \qquad \text{---------- 5,}$$

Where k is a constant, T is the absolute temperature; b is a constant equal to 2 for the liquid and the excess values of these parameters are determined by using the relation

$$A^E = A_{exp} - A_{id} \qquad \text{---------- 6,}$$

A^E - excess value of any acoustic parameters, $A_{id} = \sum_{i=1}^{n} A_i X_i$,

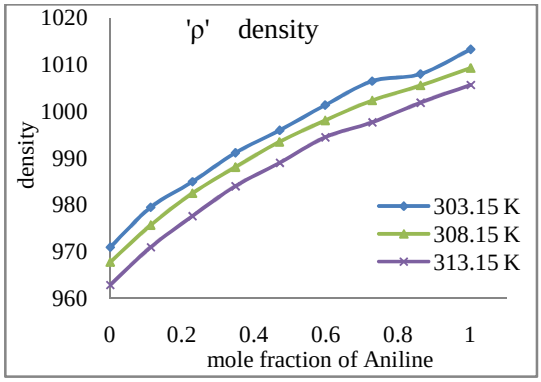
A_i is any acoustical parameter and X_i – the mole fraction of liquid component.

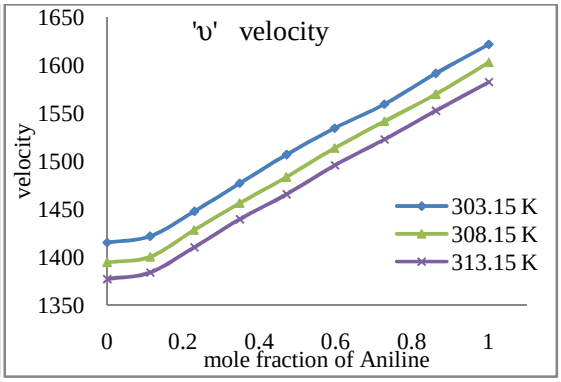
RESULTS AND DISCUSSION

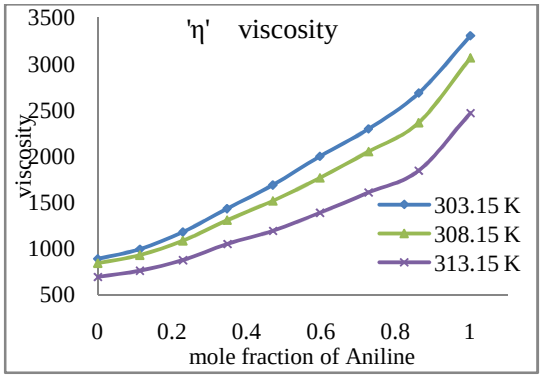
The graphical representation obtained after the measurements and evaluation of various parameters reveal that the values of ultrasonic velocity (υ) and density (ρ) increases with the concentration of Aniline in Pyridine but the adiabatic compressibility (β_α) shows the negative i.e. opposite trend than that of velocity at all temperatures. Free length (L_f) also seen to be in similar relation with the concentration as that of compressibility but the values of viscosity (η), acoustical impedance and Internal pressure (π_i) increases with the concentration of aniline in the mixture. It is clear that intermolecular free length depends upon intermolecular attractive and repulsive force[10]. The values of free volume (V_f) and internal pressure (π_i) are showing opposite nature to each other. Also the increase in temperature decreases the density, velocity is also seen to be decreasing and similarly the viscosity, but

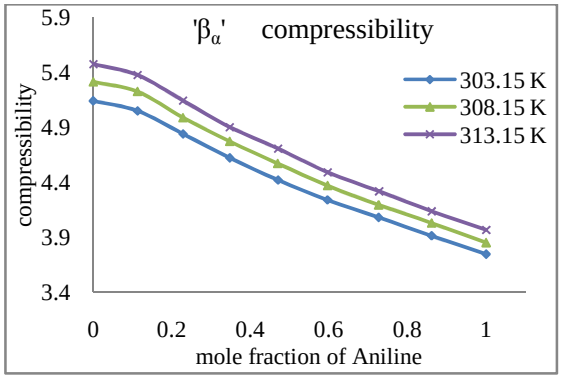
there is increase in compressibility and free length which is responsible for the increase in free volume corresponding to increase in temperature.

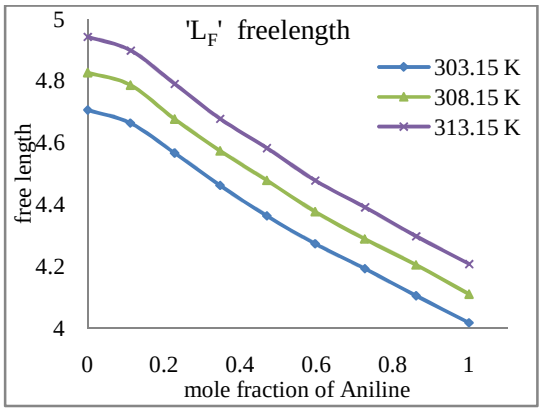
The plots of these parameters with concentrations conforms the non linear variation (figure 01-06). The values of adiabatic compressibility (β_α) and free length (L_f) decreases with increase in the concentration of Aniline. The decrease in the values of free length with increasing concentration can be concluded as there is significant interaction between the two liquids[11]. It is also observed that as the concentration of Aniline increases, free volume decreases whereas the internal pressure increases. This suggests the close packing of the molecules, which may be concluded as the increasing magnitude of the interaction[12-14]. The non linear variation in the above parameters with the mole fraction of aniline is an indication of existence of interaction between the components of the mixture[15, 16]. The viscosity values showing increasing trend is the indication of frictional resistive force that may be due to a change in effective molecular area by the cohesive or adhesive forces or relative random velocity between the components of the mixture[10].

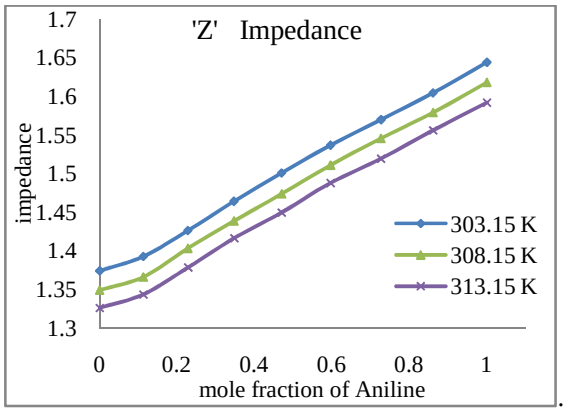












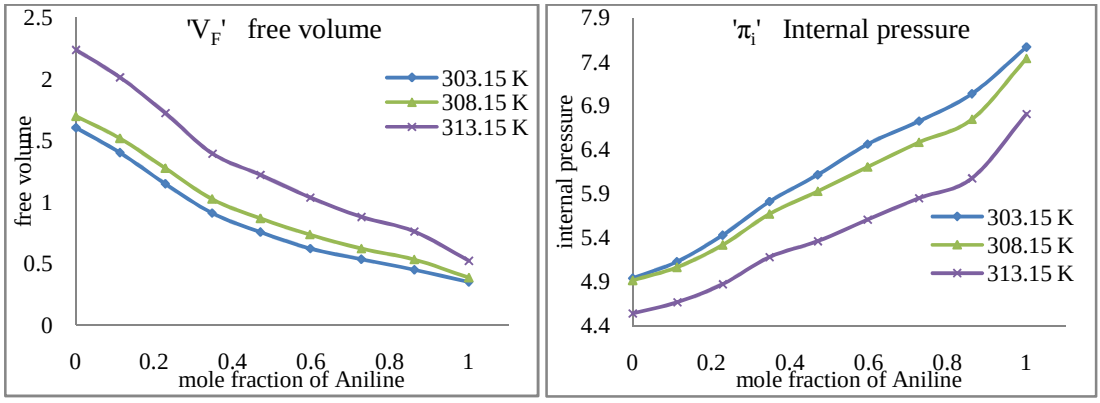
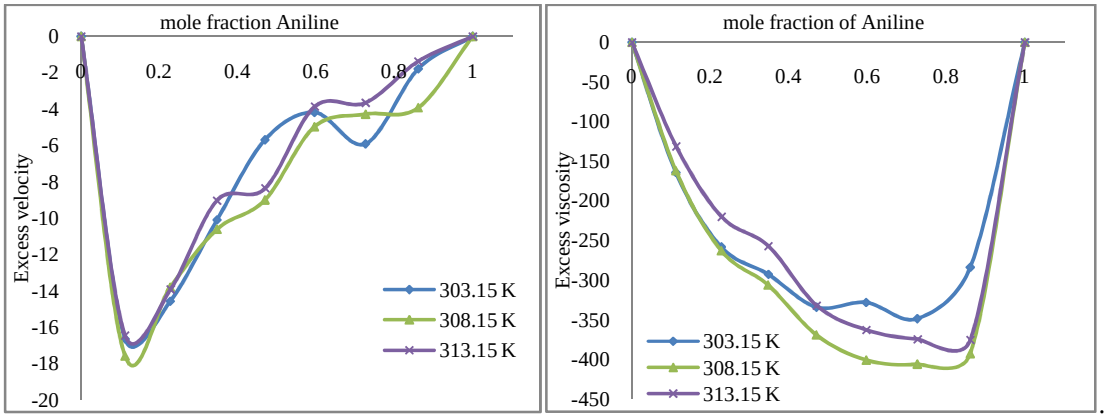


Figure 01-08. plots of ultrasonic density(ρ), velocity(υ), viscosity(η), adiabatic compressibility (β_a) free length (L_f), impedance (Z), free volume (V_f) and internal pressure (π_i) for Pyridine + Aniline mixture for different concentration of Aniline at different temperatures

The existence of any inter molecular interaction can be supplemented with the help of excess values of the thermo dynamic parameters. The extent of deviation & sign of these functions depends on the strength of interaction between unlike molecules[17, 18]. Here the excess velocity is seen to be negative which can be concluded as the making and breaking of a structure. The excess compressibility and free length shows the negative pattern and the same trend can be observed in the excess values of viscosity but the excess values of viscosity are more negative it means the strong attractive or repulsive forces are acting between the different components of the mixture. The close perusal of the excess values in the figure 07- 13, conform the trend in excess free volume and excess internal pressure.

The sign of excess free length plays a vital role in assessing compactness due to molecular interaction through dipole-dipole interaction[19,20], leading to more compact structure making which enhances excess free length to have negative values. The excess ultrasonic velocity (υ^E) for the binary mixture is negative. The similar relation is observed for the impedance.



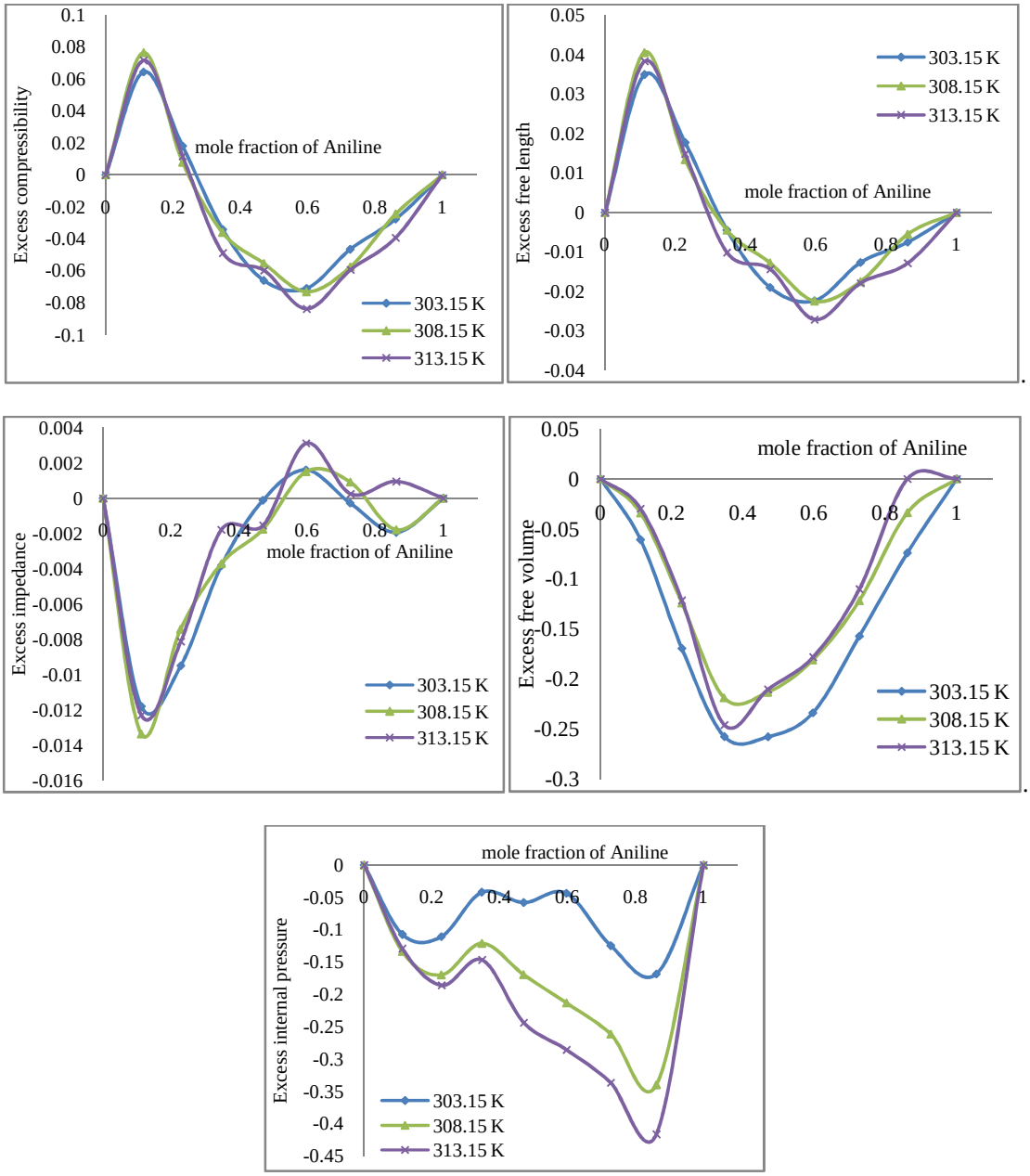


Figure 09-15. plots of excess values of ultrasonic velocity (υ), viscosity(η), adiabatic compressibility (β_a) free length (L_f), impedance (Z) free volume (V_f) and internal pressure (π_i) with their excess values for Pyridine + Aniline mixture for different concentration of Aniline at different temperatures

CONCLUSION

The present study leads to conclude that the results are very basic in nature and non linear variation of all the parameters measured at 303, 308 & 313K indicates the existence of interaction between the different molecules of the components for the mixture of Aniline and Pyridine. The non-linearity of the curve is common for all compositions. The negative values of excess ultrasonic velocity (υ^E), excess compressibility (β_α^E), excess viscosity (η^E), excess free length (L_f^E), excess impedance (Z^E), excess free volume (V_f^E) & excess internal pressure (π_i^E) for the different concentration of the aniline in the mixture conforms the presence of strong dispersive interaction between the components of molecule in the mixture. The excess values of thermodynamic parameters are sensitive

to the molecular association present in the liquid mixture which supports our conclusion. At the mole fraction of 0.2 of aniline the specific interactions are seen.

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