STUDY OF MOLECULAR INTERACTIONS IN THE BINARY LIQUID MIXTURES OF ACETOPHENONEAT DIFFERENT TEMPERATURES BY ULTRASONIC METHOD

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ABSTRACT

The state of matter that is very important in the activities of living things is liquid state. The behaviour of the molecules in this state can be easily studied and there interactions can also be understood with the help of many available methods of studies. The ultrasonic method is preferred over these all because of its simplicity and applicability to provide analysis of properties of liquids and there properties. Here the two binary systems of acetophenone one with acetone and the other with pyridine are taken for studies to find out any type of relationships between the molecules of the mixture.

The density, ultrasonic velocity with coefficient of viscosity were measured by varying concentrations and temperatures of the binary mixtures to evaluate the different parameters like compressibility, intermolecular free length, free volume, internal pressure. The evaluated excess values of the above parameters,excess velocity v^E, excess adiabatic compressibility $\beta_\alpha{}^E$, excess free volume V_f^E and excess internal pressure $\pi_i{}^E$were plotted against molar concentration at different temperatures and results were discussed for the molecular interaction. The data confirms the existence of polar interactions in both the binary mixtures.

Keywords: *Molecular interaction, free volume, ultrasonic velocity, compressibility, internal pressure, excess parameters.*

1. Introduction

The molecular behavior has very high importance in the activities of the living things. The behavior can be easily studied in the liquid state and also the liquids are very important rulers in the activities of livings and non-livings. The knowledge about the behavior of the molecules is needed in pure and applied fields of studies. Therefore the researchers are always devoted to investigate the molecular behavior by one or the other methods of studies. In spite of different research methods ultrasonic study have played an important role and found easier way to investigate into the characteristics of the molecules in the liquids and their mixture. It is well known that the velocityof ultrasonic waves depends on the molecular forces therefore it provides directly what and how about the nature of intermolecular behavior existing between the components of the liquid and its mixtures.

The liquids like acetone, pyridine and acetophenone are having many applications in the different fields of human importance like, chemical, pharmaceutical, medical, bio medical, automobile, and research. Also these liquids are having much importance to find out the type of intermolecular interactions for the chemists(Eyring,1938; Swain, 2010; Srinivasulu, 1995; Pitzer, 1995; Tabhane, 1999; Kannapan, 2009).

In view to understand the nature of molecular behavior between the components of the mixture and its liquids the ultrasonic velocity, coefficient of viscosity with the measurement of density by very simple methods and then utilize them to derive the different ultrasonic parameters helps to discuss the existence of molecular interactions in the liquid mixtures (Arul, 2005; Gupta, 1981). The results obtained are also discussed in terms of their excess values.

2. Methods and Measurements

The chemicals used here Acetophenone, Acetone and Pyridine are of 99-99.5% purity and grade AR were purchased commercially and used as it is without further purification. The two binary mixture

of acetophenoneone with pyridine and the other with acetone were prepared by adding the liquid acetophenoneseparately in the above two liquidsby varying concentration of acetophenone. The mixtures were stored in specially designed flasks to avoid any air contact. All the mixtures were utilized within the 24 hours of their preparation. The Ultrasonic Interferometer (Mittal enterprises- model M-81) with constant temperature bath is used for the measurements of Ultrasonic velocities (υ) for different concentrations and different temperatures of binary mixtures. The specific gravity bottle and mono pan balance are used to measure densities of different mixtures, and the suspended level viscometer is used to measure the coefficients of viscosities of pure liquids and their mixtures. The measured density (ρ), ultrasonic velocity (υ) and coefficient of viscosity (η) are used to evaluate various thermo-acoustical parameters and their excess values by standard relations, such as

Adiabatic compressibility:

$\beta_\alpha = 1/\upsilon^2 \rho$ ----------1

Intermolecular free length:

$L_f = K\beta_\alpha^{½}$---------- 2

Where, $K= (93.875 + 0.375\ T) \times 10^{-8}$,

K –is temperature dependent constant(Jakobson,1952)

Acoustical Impedance (Z)

$Z = \rho \upsilon$ ---------- 3

Free volume:

$V_f = [(M_{eff}/ k\eta) \upsilon]^{3/2}$ ---------- 4

The internal pressure (π_i),

$$\pi_i = bRT\left(\frac{kn}{v}\right)^{1/2}\left(\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right)$$ ---------- 5

Where,k is temperature independent constant which is equal to 4.28×10^9 for all liquids, 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

$A^E = A_{exp} - A_{id}$ ---------- 6

where, 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.

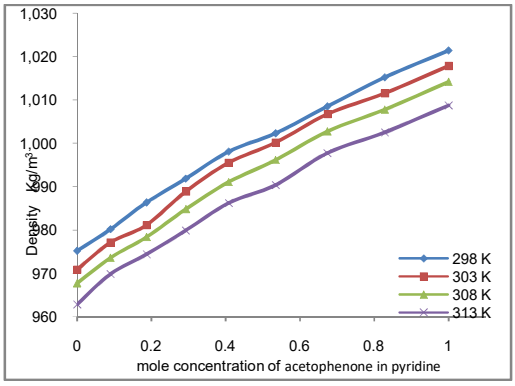
3. Result and Discussion

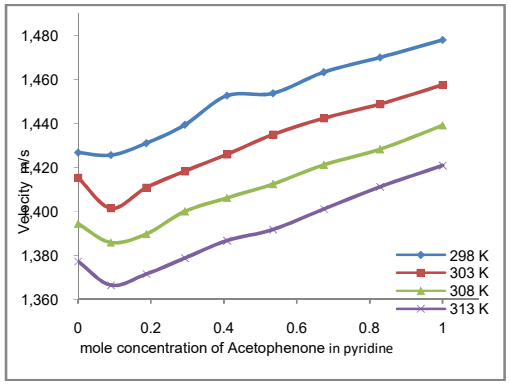
The binary mixtures under investigation were prepared by adding the liquid acetophenone with increasing concentration in the liquid pyridine for first binary mixture and in acetone to prepare second binary mixture.Thedensity of acetophenoneis more than the density of pyridine as well as acetone therefore any increase in the concentration of acetophenone in the respective binary mixtures increases the overall density of these mixtures. The value of ultrasonic velocity (υ) and coefficient of viscosity (η) are found to increase in the binary mixtureswith the increase in concentration of acetophenone in pyridineas well as acetone in their respective mixtures. The adiabatic compressibility (β_α), intermolecular free length (L_f) and free volume (V_f)shows the opposite trend to that of acoustical velocity at the four different temperatures 298, 303, 308 and 313K for both the liquids. The increasing trend in coefficient of viscosity is the indication of existence of frictional resistive forces that may be due to a change in effective molecular area and due to the existence of cohesive or adhesive forces between the molecules. The intermolecular free length is a parameter that is also related with the forces depends upon intermolecular attractive and repulsive forces (Banipal, 2000; Naidu, 2002). Then any type of decrease in free length is responsible for the decrease in free volume of the mixture which also ultimately responsible for the increases the internal pressure of the system which is observed in the system with acetone but lowered in the system with pyridine this may be because of some kind of electrostatic forces between the molecules of pyridine and acetophenone, these results are confirmed from the plots of

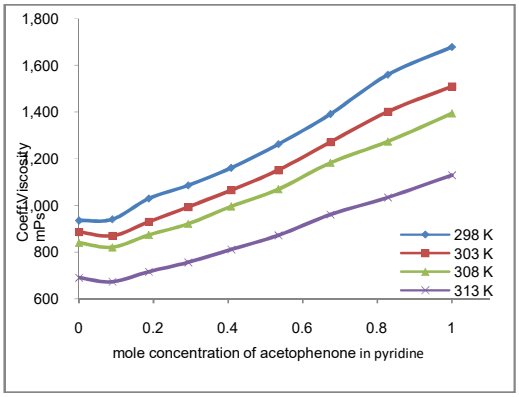
these all parameters (figure 01-07) and (figure 14 to 20). The observed decrease in the values of free length and free volume can be concluded as the existence of significant interaction between the two binary mixtures. It also suggests the presence of close packing of the molecules (Kannapan, 1991; Arul, 2001; Redlich, 1948). The changes in the free volume and the internal pressure are also plotted as a function of concentration of acetophenone for different temperatures. The increase in the temperature of the mixture decreases the density of the binary mixture which is the basic property of the liquid. The increase in the temperature of the binary mixture decreases the velocity and coefficient of viscosity but the compressibility of the liquid and its mixture increases this is observed for both the systems under study. The free volume and free lengths are found to be increasing with the increase in temperature of the system this is due to the increase in molecular energy and the separation, all this concludes the existence of some kind of molecular interactions between the components of the mixture and these kind of interactions are associative. Therefore the internal pressure in both the binary mixtures decreases with the increase in temperature of the system.

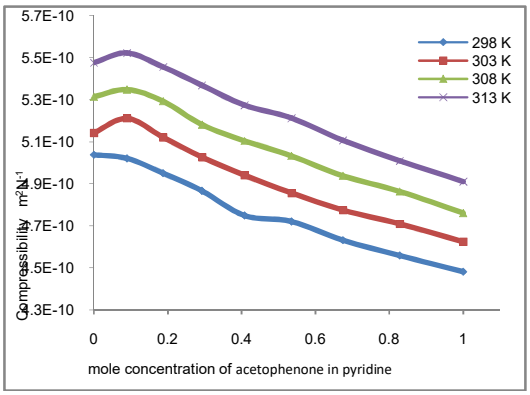
The extent of deviation & sign of excess values of the thermo dynamical parameters depends on the strength of interaction between molecules (figure 08 to 13) and (figure 21 to 26). The excess velocity is seen to be negative which can be concluded as the making and breaking of the structure in the both systems (Rao, 2002; Anbabathan, 1979; Ali, 1999). Excess velocity for the binary mixture of pyridine with acetophenone at temperature 298 K shows positive value at 0.4 concentration which is because of some kind of molecular interactions at that concentration and can be attribute to have interactions between the molecules of the system. The excess values of coefficient of viscosity and excess internal pressure are observed to be negative for our first system i.e. pyridine and acetophenone and other excess parameters of free volume free length and compressibility are positive which again confirms the polar and non- polar interactions with the molecules, in the second system i.e. acetone with acetophenone the excess values of the parameters viscosity, compressibility, free length and free volume and internal pressure also have negative values which indicates the presence of strong interaction between the components of the mixture. The sign of excess free length plays a vital role in assessing compactness due to molecular interaction through dipole-dipole interaction. The increase in compactness enhances structure making and excess free length tends to negative values. Excess compressibility and excess free length are negative indicates the weak and strong interactions are prevailing in the present binary mixtures (Dabrase, 2013; Praharaj, 2012; Dabrase, 2012 & 2015).

Figures






Coeff.Viscosity mPs
mole concentration of acetophenone in pyridine
298 K
303 K
308 K
313 K


Compressibility m²N⁻¹
mole concentration of acetophenone in pyridine
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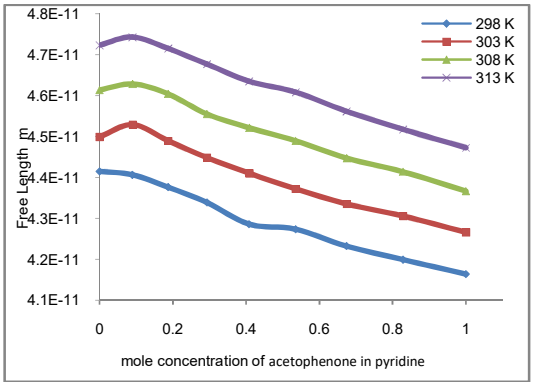
308 K
313 K


Free Length m
mole concentration of acetophenone in pyridine
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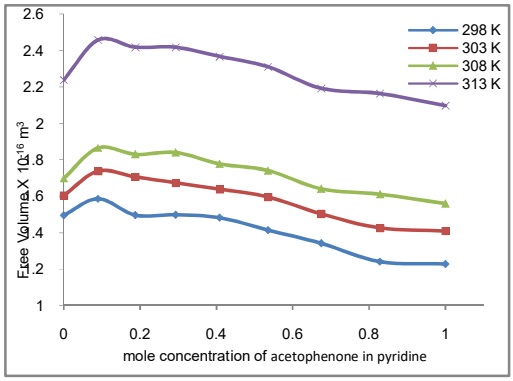
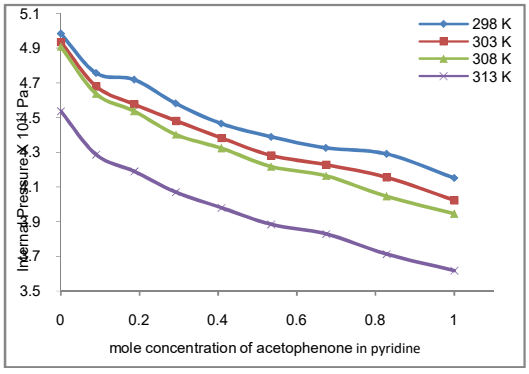
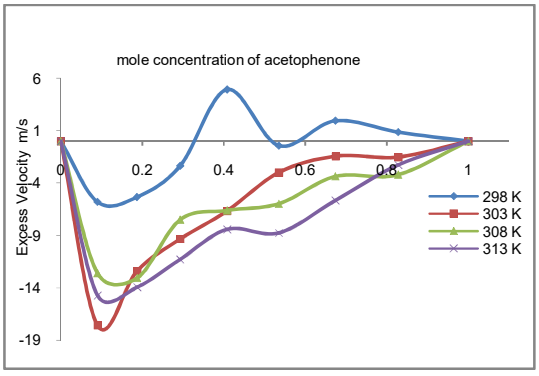
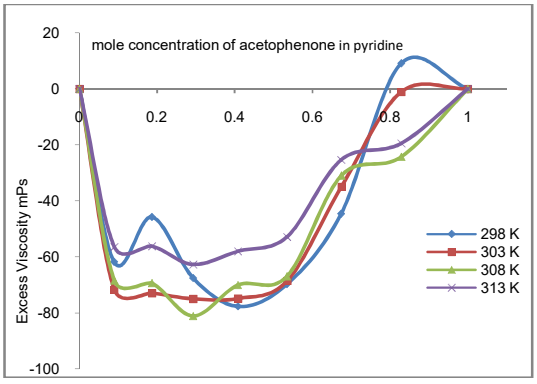
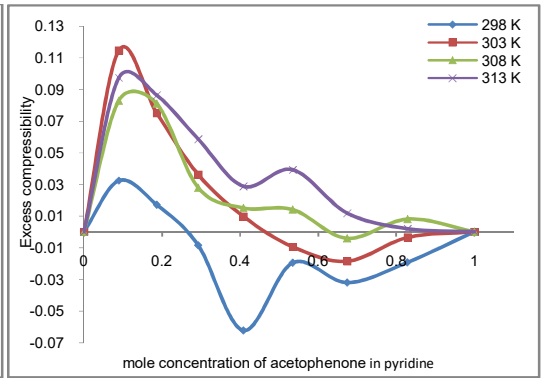
303 K
308 K
313 K

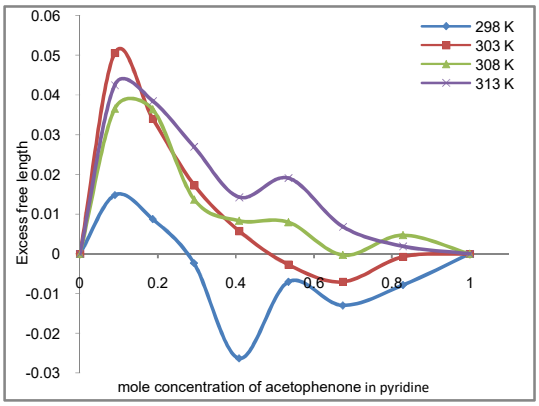

Free Volume X 10⁻¹⁶ m³
mole concentration of acetophenone in pyridine
298 K
303 K
308 K
313 K

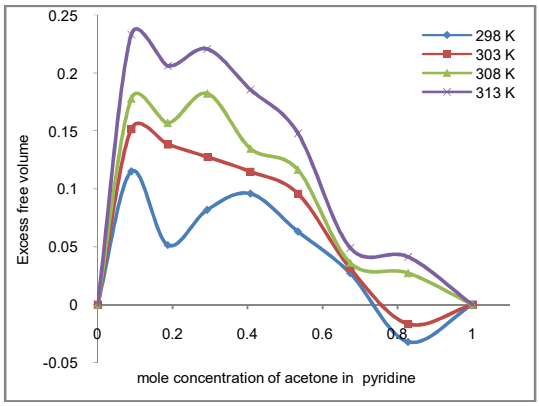

Internal Pressure X 10⁻⁴ Pa
mole concentration of acetophenone in pyridine
298 K
303 K
308 K
313 K


mole concentration of acetophenone
Excess Velocity m/s
298 K
303 K
308 K
313 K


mole concentration of acetophenone in pyridine
Excess Viscosity mPs
298 K
303 K
308 K
313 K


Excess compressibility
mole concentration of acetophenone in pyridine
298 K
303 K
308 K
313 K





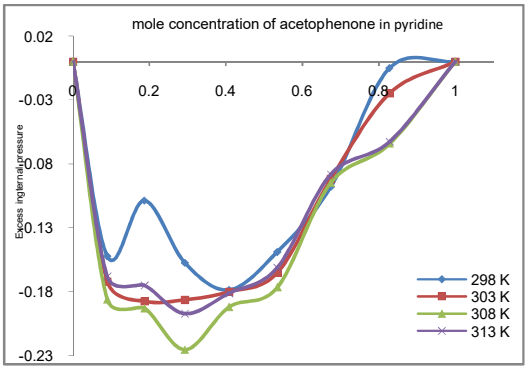
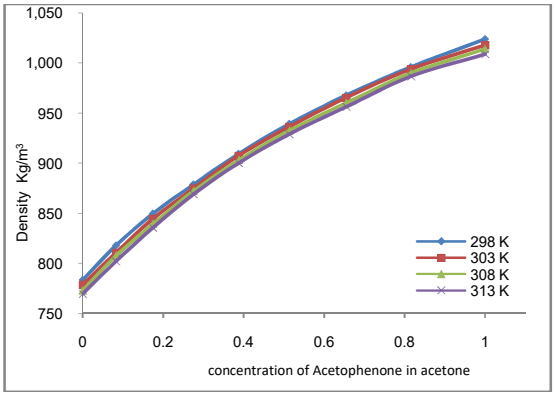
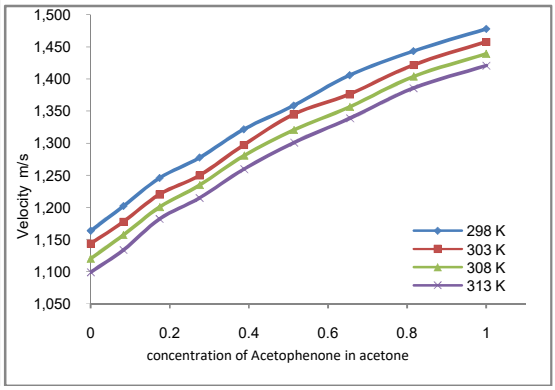
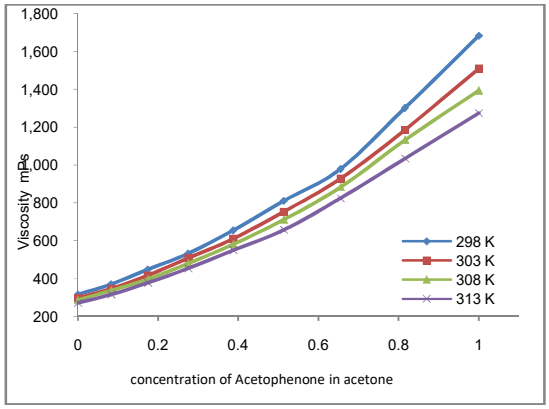
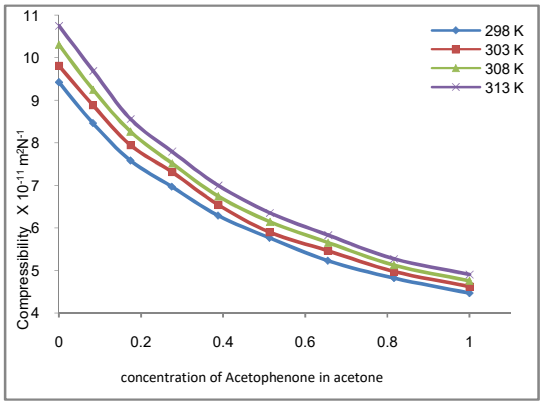


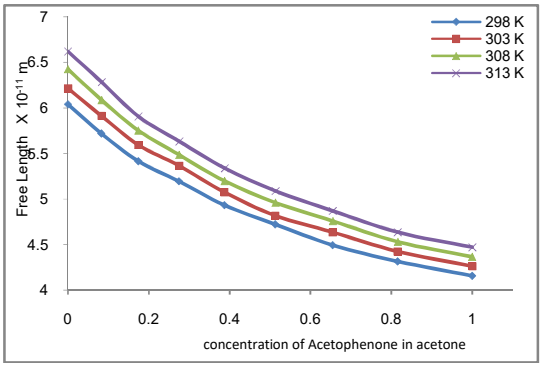
Figure:(1 to 13):
Plots of ultrasonic velocity, viscosity, adiabatic compressibility, free length, free volume and internal pressure and their excess values for varying concentration of acetophenone in pyridine at 298, 303, 308 and 313K temperatures.

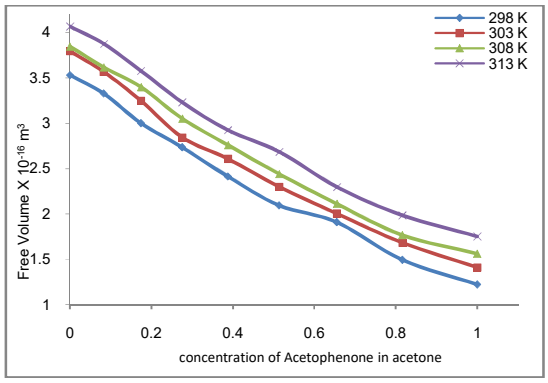


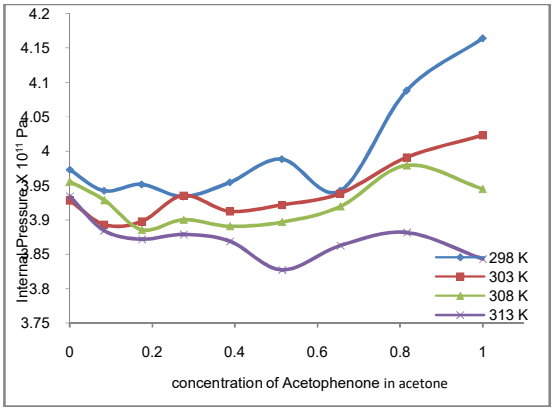


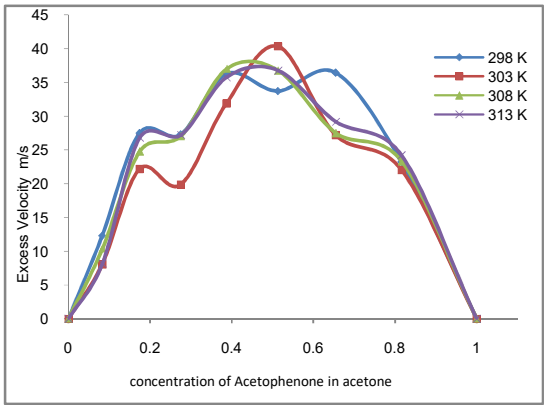


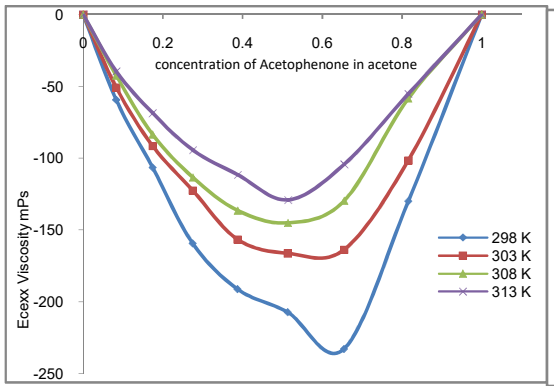


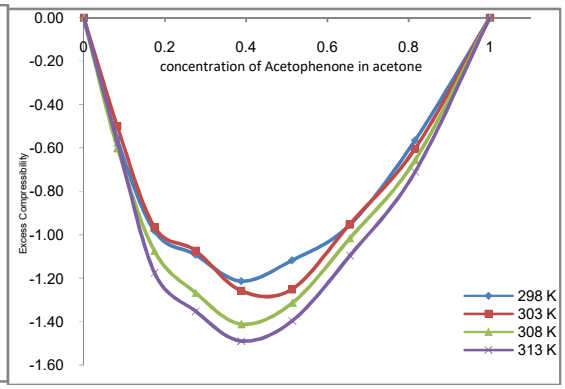

Free Length X 10^-11 m
concentration of Acetophenone in acetone
298 K
303 K
308 K
313 K

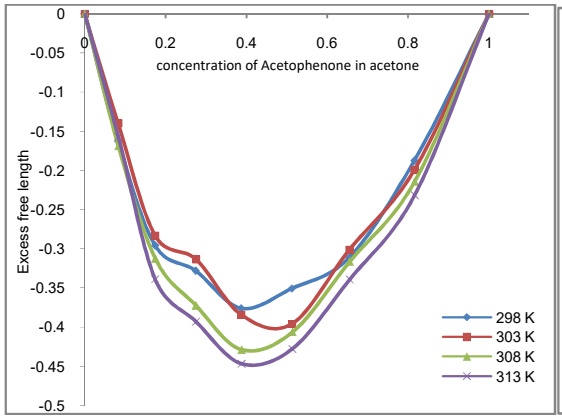

Free Volume X 10^-16 m^3
concentration of Acetophenone in acetone
298 K
303 K
308 K
313 K

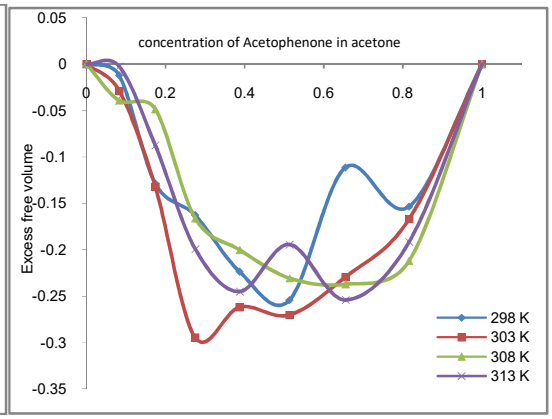

Internal Pressure X 10^11 Pa
concentration of Acetophenone in acetone
298 K
303 K
308 K
313 K


Excess Velocity m/s
concentration of Acetophenone in acetone
298 K
303 K
308 K
313 K


Ecexx Viscosity mPs
concentration of Acetophenone in acetone
298 K
303 K
308 K
313 K


Excess Compressibility
concentration of Acetophenone in acetone
298 K
303 K
308 K
313 K


Excess free length
concentration of Acetophenone in acetone
298 K
303 K
308 K
313 K


Excess free volume
concentration of Acetophenone in acetone
298 K
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308 K
313 K

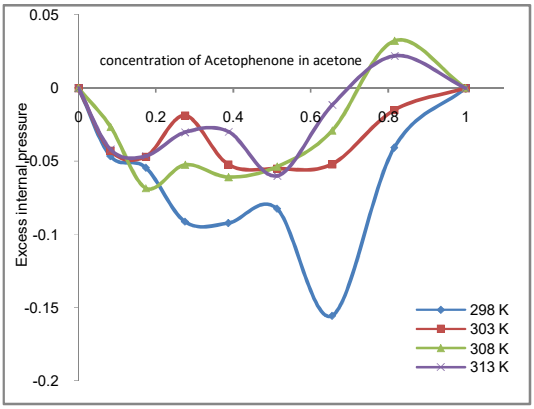

Figure: (14 to 26):
Plots of ultrasonic velocity, viscosity, adiabatic compressibility, free length, free volume and internal pressure and their excess values for varying concentration of acetophenone in acetone at 298, 303, 308 and 313K temperatures.

4. Conclusion

In the binary mixtures of acetophenone one with pyridine and second with acetone, the increase in the values of density,ultrasonic velocity and coefficient of viscosity and the internal pressure for the increase in concentration of acetophenone in the respective mixturesand the decreasing values of adiabatic compressibility, intermolecular free length and free volume for the increase in concentration of acetophenonein that mixtures confirms the existence of intermolecular interactions between the different components of the mixture. The internal pressure in the first system of pyridine and acetophenoneconfirms the associative and dissociative interactions between the molecules of the system. The negative excess values of ultrasonic velocity (υ^E) andcoefficient of viscosity (η^E), in the first system of pyridine and acetophenone. Positive excess values of ultrasonic velocity (υ^E) and negative excess values of viscosity (η^E), excess free volume (V_f^E), the excess compressibility (β_α^E) and excess free length (L_f^E) withnon- linearityat temperatures 298, 303, 308 and 313K indicates the polar and non–polar interactions in the second system. More negative excess internal pressure (π_i^E) in the binary mixture confirms the presence of strong dispersive interaction between the components of molecule. The non-linear variation of all the parameters is the indicator of existence of dipole-dipole interactions between the different molecules present in the binary systems. Thus some differences in the kinds of interactions are present in these two binary liquid systems.

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