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Research Paper

Thermodynamics and Transport Properties of Ester with Cyclohexane in Pentanol at 303, 308 and 313K

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Abstract: *The ultrasonic velocity (U), density (ρ), viscosity (η) have been measured for the ternary mixtures of Methyl Benzoate and Cyclohexane with Pentanol at 303, 308 and 313K. From the experimental data, Adiabatic Compressibility (β), Free Length (L_F), Free Volume (V_F), Internal Pressure (π_i), Relaxation time (τ), Acoustic Impedance (Z), Gibbs Free Energy (ΔG), Classical Absorption Coefficient (d/f^2) and Cohesive Energy (H) have been calculated. In addition to that the excess values of certain above parameters are also evaluated. The excess properties have been used to discuss the presence of significant interactions between the component molecules in the ternary mixtures.*

Keywords: Density, Viscosity, Adiabatic Compressibility, Excess values.

Introduction

The study of intermolecular interaction plays an important role in the development of molecular sciences. A large number of studies have been made on the molecular interaction in liquid systems by various physical methods like Infrared [1,2], Raman effect [3,4], Nuclear Magnetic resonance, Dielectric constant[5], ultra violet[6] and ultrasonic method [7,8]. In recent years ultrasonic technique has become a powerful tool in providing information regarding the molecular behavior of liquids and solids owing to its ability of characterizing physiochemical behavior of the medium.

The present investigation deals with the study of molecular interaction in ternary liquid mixtures (Methyl Benzoate+ Cyclohexane + Pentanol at different temperature). The physical and chemical properties of liquid mixtures have been studied by numbers of workers [9,10] and they correlated the non-linear variation of ultrasonic velocity, compressibility and other related parameters with structural changes occurring in a liquid as its concentration is varied in a liquid mixture.The intermolecular forces responsible for the molecular interactions can be classified as long range forces and Short range forces.

The long range forces are the electrostatic and dispersion forces and they arise when the molecules come close enough together causing a significant overlap of electron clouds and are often highly directional. The non-linear variation of adiabatic compressibility of the solution with concentration of the solute was qualitatively described to hydrogen bonding and their result confirms that the sign and magnitude of such deviation depends on the strength of interaction between unlike molecules. Though spectroscopic methods play a major role in the molecular interaction studies, the non-spectral studies such as calorimetric, magnetic, ultrasonic velocity and viscosity measurements have also been widely used in the elucidation of the formation of complexes.

Methyl benzoate is an ester, reacts with acids to liberate heat along with alcohols and acids, and it is used as a source of benzoyl radical. Cyclohexane is non - polar, it is a solvent and it is used in the production of nylon. Pentanol (or n-Pentanol, pentan-1-ol), is an alcohol with five carbon atoms and the molecular formula $C_5H_{12}O$.

Pentanol is a colorless liquid with an unpleasant aroma. Pentanol can be used as a solvent for coating CDs and DVDs. Therefore in order to have a clear understanding of

the intermolecular interactions between the component molecules, a thorough study on the liquid mixtures using ultrasonic velocity data has been performed.

Material and Methods

All the chemicals used in the present work are Analar grade. The purity of the chemicals was ascertained by comparing their densities, viscosities and ultrasonic velocities at 303, 308 and 313K which agrees with the corresponding literature values. The mixtures of Methyl Benzoate+ Cyclohaxane+ Pentanol were prepared by weight. The mole fraction of the second component, Cyclohexane (x_2=0.4) was kept constant, while the mole fractions of the remaining two (x_1, x_3) were varied from 0.1 to 0.6.The ultrasonic velocity was measured by a single crystal interferometer with a high degree of accuracy operating at a frequency of 3 MHz (model F-05, with digital micrometer) at 303, 308 and 313K. The viscosity was measured by Ostwald's viscometer. An electronically operated constant temperature water bath is used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature. Densities of the mixtures have been found by relative measurement method.

Calculation

Intermolecular free length (L_F) is calculated using the standard expression

$$L_F = K \beta^{1/2} \quad (1)$$

where K is a temperature dependent constant known as Jacobson constant and β is the adiabatic compressibility that can be calculated from the speed of sound (U) and the density of the medium (ρ) as

$$\beta = \frac{1}{U^2 \rho} \quad (2)$$

The relation for free volume in terms of ultrasonic velocity (U) and the viscosity (η) of the liquid as

$$V_F = \left(\frac{M_{eff}\, U}{\eta K}\right)^{3/2} \quad (3)$$

Expression for the determination of internal pressure (π_i) by the use of free volume (V_F) as

$$\pi_i = bRT \left(\frac{K\eta}{U}\right)^{1/2} \left(\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right) \quad (4)$$

where b stands for cubic packing which is assumed to be 2 for liquids and K is a dimensionless constant independent of temperature and nature of liquids and its value is 4.281×10^9, T is the absolute temperature and M_{eff} is the effective molecular weight.

Relaxation time (τ) can be calculated using viscosity and adiabatic compressibility

$$\tau = \frac{4}{3} \eta\beta \quad (5)$$

Acoustic Impedance $Z = \rho U$ (6)

where ρ is the density

U is the ultrasonic velocity

Gibb's Free Energy $\Delta G = K_B\, T\, \ln\left(\frac{K_B\, T\, \tau}{h}\right)$ (7)

where $K_B = 1.23 \times 10^{-23}$ J/K

t is the temperature

τ is the relaxation time

$h = 6.626 \times 10^{-34}$ Js (Planck's Constant)

Classical Absorption coefficient is calculated by the formula

$$\frac{d}{f^2} = \frac{8\pi^2 \eta}{3 U^2 \rho} \quad (8)$$

where η is the viscosity of the liquid and ρ is the density of the liquid

Cohesive energy (H) is given by

$$H = \pi_i \left(\frac{M_{eff}}{\rho}\right) \quad (9)$$

where π_i is the Internal Pressure and M_{eff} is effective molecular weight

In order to study the non-ideality of the liquid mixtures, namely excess parameters (A^E) of all the acoustic parameter were computed by

$$A^E = A_{exp} - A_{id} \quad (10)$$

where $A_{id} = \sum A_i X_i$ (11)

A_i is any acoustical parameter and x_i is the mole fraction of the liquid components.

Results and Discussion

Table 1 represents the variation of mole fraction versus experimentally measured values of density (ρ), viscosity(η) and ultrasonic velocity(U) of the mixtures at 303, 308 and 313k. Table 2 represents the variation of Adiabatic Compressibility (β), Free Length (L_F), Free Volume (V_F) and Table 3 represents Internal Pressure(π_i), Relaxation time(τ), acoustical impedance(Z). Table 4 represents Gibbs free energy (ΔG), Classical Absorption Coefficient (d/f^2) and Cohesive Energy (H) for the mixtures. Excess values are depicted in Table 5.

From the Table (1) it was observed that the ultrasonic velocity, density of the ternary liquid mixtures decreases with increasing mole fraction of Pentanol while the

viscosity increases. However, the ultrasonic velocity, density, viscosity decreases in all the cases as temperature increases. The same result was obtained by A. N. Kannappan et al[7,8].

Table 1
Density (ρ), viscosity (η) and velocity (U) of Methyl Benzoate, Cyclohexane and Pentanol at 303, 308 and 313K

x_1	x_3	ρ Kg/m^3			η x 10^{-3} Ns/m^2			U (m/s)		
		303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K
0.60	0.00	957.90	957.00	953.00	0.93	0.88	0.84	1282.80	1270.00	1246.00
0.50	0.10	937.96	935.93	932.29	1.11	1.00	0.95	1356.70	1315.30	1301.00
0.40	0.20	910.34	904.66	901.01	1.13	1.03	0.96	1326.00	1290.00	1281.00
0.30	0.30	878.65	875.84	873.38	1.14	1.03	0.98	1296.40	1253.70	1224.40
0.20	0.40	853.87	846.60	842.51	1.14	1.08	1.00	1260.90	1234.00	1217.40
0.10	0.50	823.00	816.15	813.26	1.23	1.11	1.06	1226.00	1212.00	1188.20
0.00	0.59	790.50	787.32	783.61	1.53	1.45	1.33	1214.00	1205.00	1200.00

Table 2: Adiabatic compressibility (β), free length (L_F) and free volume (V_F) of Methyl Benzoate, Cyclohexane and Pentanol at 303, 308and 313K

x_1	x_3	Adiabatic compressibility			Free length			Free Volume		
		β x 10 $^{-10}$ m^2/N			L_F x 10^{-10} m			V_F x 10 $^{-7}$ m^3 mol $^{-1}$		
		303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K
0.60	0.00	6.34	6.48	6.76	0.50	0.51	0.53	2.25	2.41	2.52
0.50	0.10	5.79	6.18	6.34	0.48	0.50	0.51	1.78	1.99	2.09
0.40	0.20	6.25	6.64	6.76	0.50	0.52	0.53	1.57	1.73	1.90
0.30	0.30	6.77	7.26	7.64	0.52	0.54	0.56	1.39	1.54	1.60
0.20	0.40	7.37	7.76	8.01	0.54	0.56	0.57	1.23	1.30	1.42
0.10	0.50	8.08	8.34	8.71	0.57	0.58	0.60	0.98	1.12	1.17
0.00	0.59	8.58	8.75	8.86	0.58	0.59	0.60	0.64	0.69	0.78

Further the adiabatic compressibility, Free Length shows an inverse behavior compared to the ultrasonic velocity in the mixtures, as shown in Figure (4, 5). It is primarily the compressibility that changes with the structure and this lead to the change in ultrasonic velocity.

The addition of interacting molecules breaks up the molecular clustering of the other releasing several dipoles for the interactions. In view of greater force of interaction between the molecules there will be an increase in cohesive energy and the occurrence of structural changes takes place due to the existence of electrostatic field.

Thus structural arrangement of molecules results in change adiabatic compressibility thereby showing progressively intermolecular interactions. Similar results in some liquid mixtures were also reported by others [12].

From tables (2, 3) it was observed that as the concentration of primary alcohol increases, free volume decreases. Internal pressure increases with increase in concentration. However, with rise in temperature increase in free volume and decrease in internal pressure are noticed. This suggests that the closed packing of molecules inside the shield. From the table (4) Gibbs Free Energy, Classical Absorption Coefficient and Cohesive Energy are increases with the increase value of mole fraction. This shows that there is a strong interaction between the mixture.

In order to understand more about the nature of the interaction between the components of liquid mixture, it is necessary to discuss the same in terms of excess parameters rather than the actual values. They can yield an idea about the non linearity of the system as association or other type of interactions [9]. The variation of excess parameters versus mole fraction of alcohol have been depicted form the Figure (13-16).

Sridevi et al [13] suggested that the negative excess compressibility has been due to closed packed molecules and positive excess values are due to weak interaction between the unlike molecules. Similar conclusions were also arrived by [14]. From the table (5) The excess properties were found to decrease with increase in temperature.

The value of excess inter molecular free length

follows the same trend as that of excess adiabatic compressibility. The value of excess inter molecular free length are negative.

The negative deviations of excess free volume are an indication of the existence of the strong interaction between the components [14]. The negative excess internal pressure over the entire range of mole fraction of the system also supports the presence of interaction.

Conclusion

The results obtained for the present study indicate that the thermodynamic parameters are sensitive to the molecular interactive present in liquid mixtures. From Ultrasonic velocity and related acoustical parameters for ternary mixtures of Pentanol with Methyl Benzoate in Cyclohexane at different concentrations and at varying temperature, it is concluded that there exists a strong molecular interaction between mixtures due to hydrogen bonding.

Acknowledgement

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Table 3
Internal Pressure (π_i), Relaxation time (τ) and acoustical impedance (Z) of Methyl Benzoate, Cyclohexane and Pentanol at 303, 308 and 313K

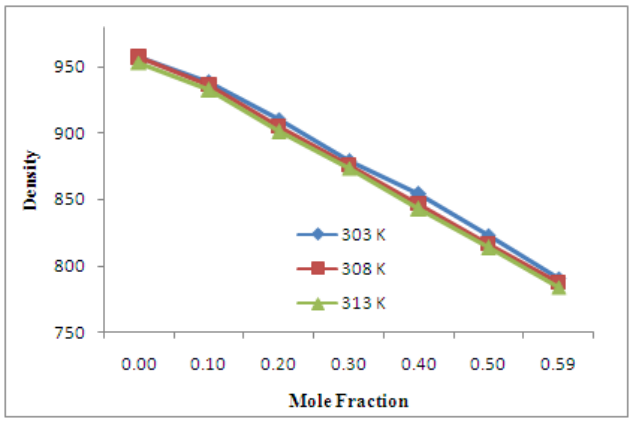
x_1	x_3	Internal Pressure π_i			Relaxation time			Acoustic Impedance		
		π_i x 10^6 N/ m^2			τ x 10^{-12} Sec			Z x 10^{-6} Kgm^2/sec		
		303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K
0.60	0.00	339.93	337.30	336.73	0.79	0.76	0.76	1.23	1.22	1.19
0.50	0.10	372.48	364.61	363.17	0.85	0.82	0.80	1.27	1.23	1.21
0.40	0.20	392.52	384.51	377.88	0.94	0.91	0.86	1.21	1.17	1.15
0.30	0.30	411.45	403.86	403.70	1.03	1.00	1.00	1.14	1.10	1.07
0.20	0.40	434.27	431.27	423.60	1.12	1.12	1.07	1.08	1.04	1.03
0.10	0.50	473.87	457.13	456.86	1.33	1.24	1.23	1.01	0.99	0.97
0.00	0.59	549.98	544.98	528.98	1.75	1.69	1.57	0.96	0.95	0.94

Table 4
Gibbs Free Energy(ΔG), Classical Absorption Coefficient (d/f^2) and Cohesive Energy(H) of Methyl Benzoate,Cyclohexane and Pentanol at 303, 308and 313K

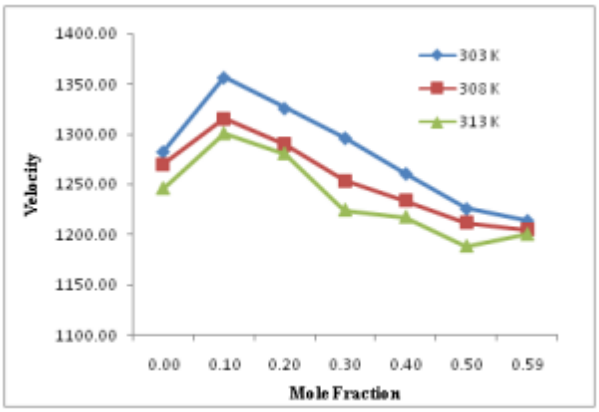
x_1	x_3	Gibbs Free Energy			Classical Absorption Coefficient (d/f2)			Cohesive Energy		
		(ΔG) x 10^{-20} KJ/mol			(d/f^2)x 10^{-11}			(H)x 10^3		
		303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K
0.60	0.00	0.56	0.56	0.57	1.56	1.50	1.49	40.91	40.64	40.54
0.50	0.10	0.58	0.59	0.59	1.68	1.62	1.59	43.90	43.07	43.06
0.40	0.20	0.62	0.62	0.63	1.85	1.79	1.70	45.60	44.95	44.35
0.30	0.30	0.65	0.66	0.68	2.03	1.97	1.96	47.27	46.55	45.66
0.20	0.40	0.69	0.70	0.70	2.22	2.20	2.11	49.90	48.98	48.34
0.10	0.50	0.74	0.75	0.76	2.62	2.44	2.42	52.60	51.16	50.31
0.00	0.59	0.85	0.86	0.86	3.45	3.34	3.09	60.20	59.89	58.41

Table 5
Excess Adiabatic compressibility (β^E), Excess Free length (L_f^E), Excess Free Volume (V_f^E) and Excess Internal Pressure (π_i^E) of Methyl Benzoate, Cyclohexane and Pentanol at 303, 308 and 313K

x_1	x_3	Excess Adiabatic compressibility			Excess Free length			Excess Free Volume			Excess Internal Pressure		
		β^E x 10^{-10} m^2/N			L_f^E x 10^{-10} m			V_f^E x 10^{-7} m^3 mol^{-1}			π_i^E x 10^6 N/m^2		
		303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K
0.6	0	-0.16	-0.32	-0.34	0.00	-0.01	-0.01	0.72	0.74	0.67	-49.12	-45.81	-38.25
0.5	0.1	-0.99	-1.04	-1.04	-0.04	-0.03	-0.04	0.37	0.43	0.36	-50.56	-48.86	-39.93
0.4	0.2	-0.81	-0.82	-0.90	-0.03	-0.02	-0.03	0.27	0.29	0.29	-64.61	-59.41	-53.43
0.3	0.3	-0.57	-0.44	-0.31	-0.02	-0.01	-0.01	0.21	0.21	0.13	-79.76	-70.50	-55.82
0.2	0.4	-0.25	-0.19	-0.22	-0.01	0.00	-0.01	0.17	0.09	0.08	-91.03	-73.54	-64.13
0.1	0.5	0.19	0.16	0.21	0.01	0.01	0.01	0.03	0.03	-0.05	-85.42	-78.04	-59.00
0	0.6	0.41	0.32	0.07	0.01	0.01	0.00	-0.20	-0.29	-0.32	-41.75	-19.11	-13.68

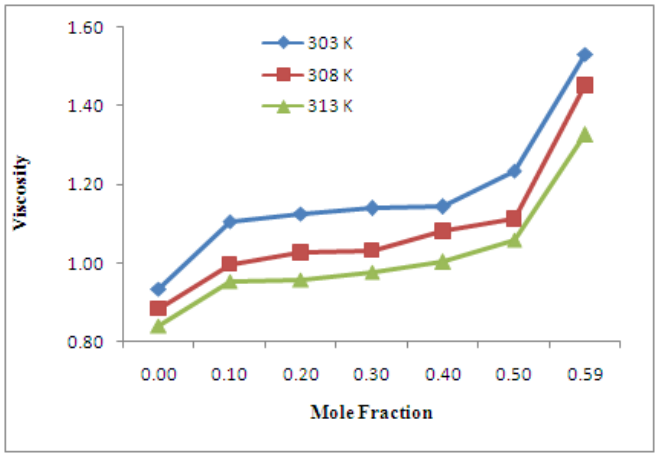


Figure(1)

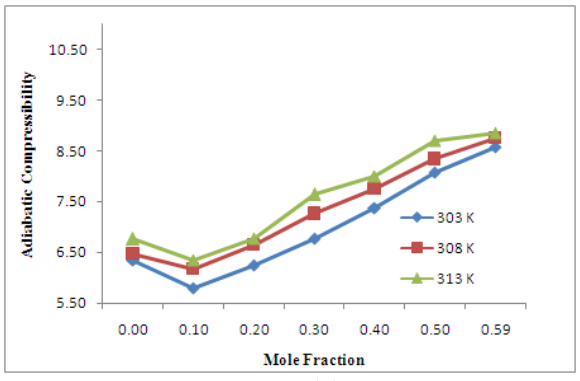


Figure(3)

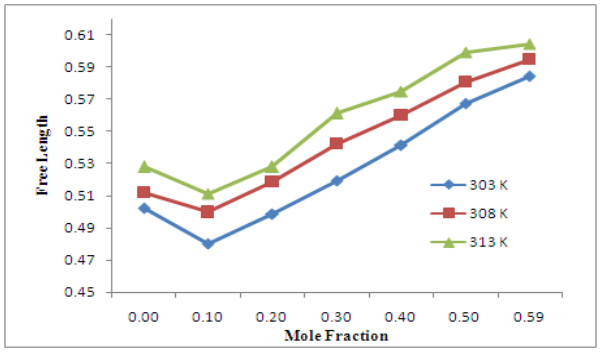
Figure 1-3. Variation of Density, Viscosity, Velocity Versus Mole fraction of (Methyl Benzoate + Cyclohexane + Pentanol) at 303, 308, 313K.



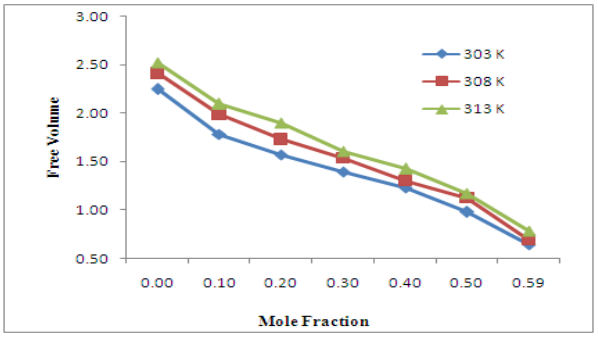
Figure(2)



Figure(4)

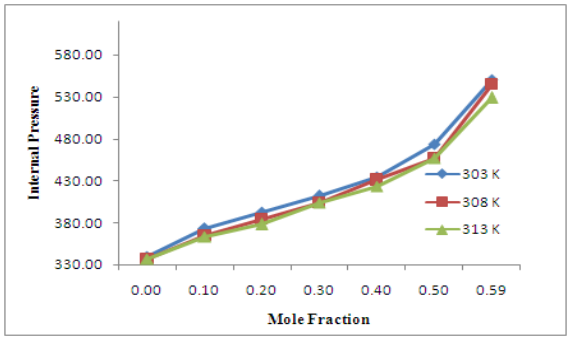


Figure(5)

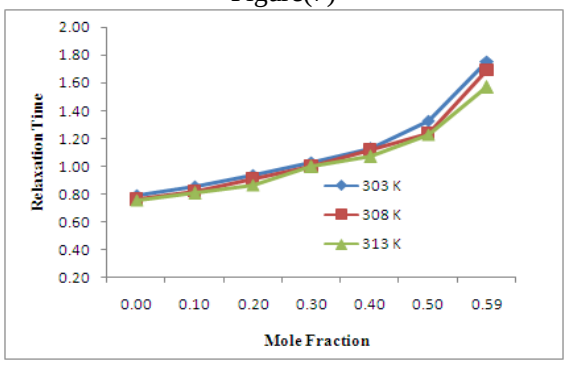


Figure(6)

Figure (4-6). Variation of Adiabatic Compressibility, Free Length ,Free Volume Versus Mole fraction of (Methyl Benzoate + Cyclohexane + Pentanol) at 303,308,313K



Figure(7)



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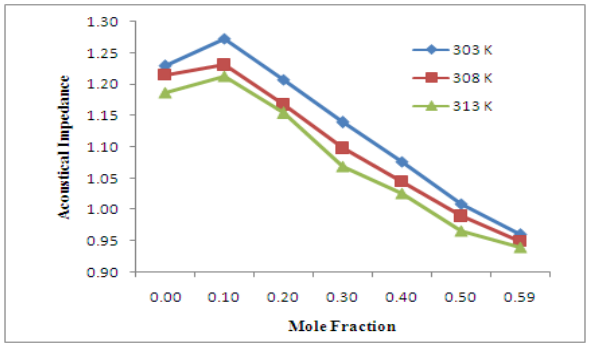
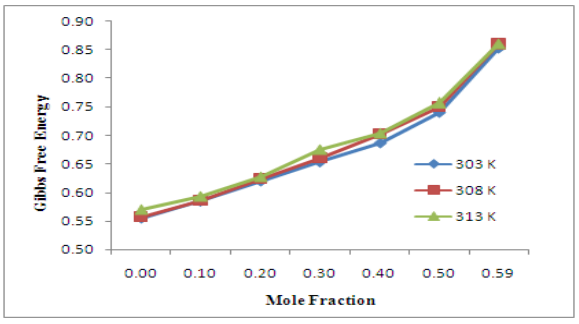
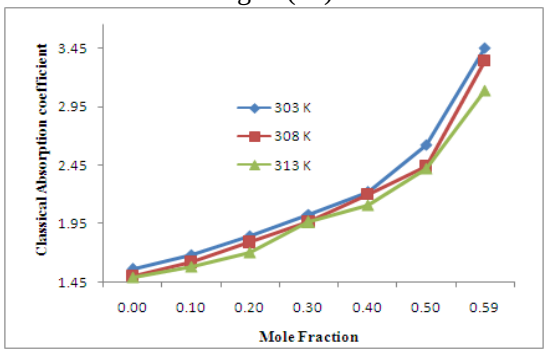


Figure(9)

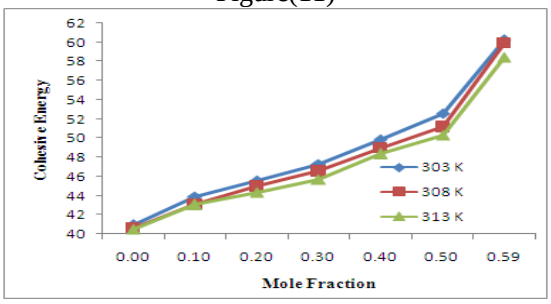
Figure (7-9). Variation of Internal Pressure,Relaxation Time,Acoustical Impedance Versus Mole fraction of (Methyl Benzoate + Cyclohexane + Pentanol) at 303,308,313K.



Figure(10)

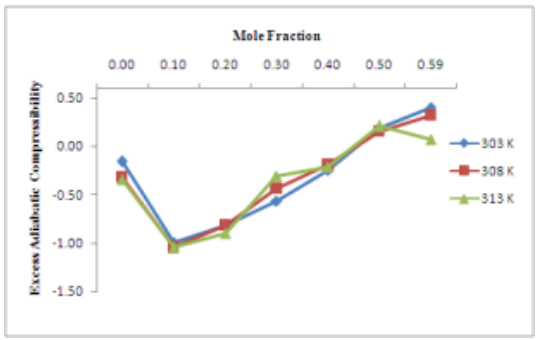


Figure(11)



Figure(12)

Figure (10-12). Variation of Gibbs Free Energy,Classical Absorption Coefficient,Cohesive Energy Versus Mole fraction of (Methyl Benzoate + Cyclohexane + Pentanol) at 303,308,313K.



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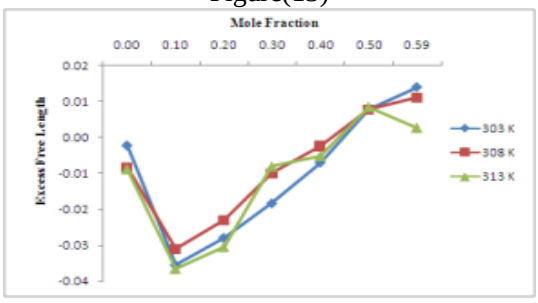

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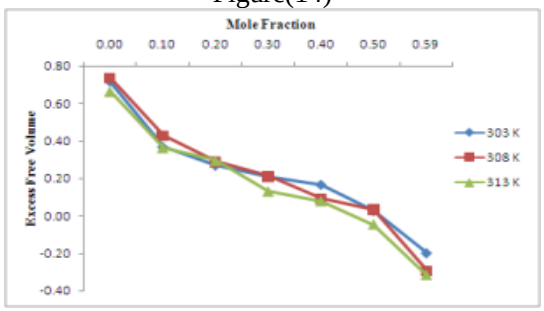

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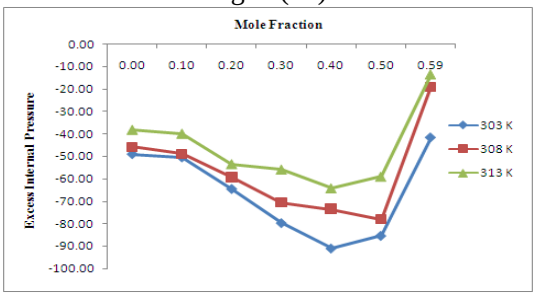

Figure(16)

Figure (12-16). Variation of Excess Adiabatic Compressibility, Excess Free Length, Excess Free Volume,Excess Internal Pressure Versus Mole fraction of (Methyl Benzoate + Cyclohexane + Pentanol) at 303,308,313K

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