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Acoustic study of Heavy fuel oil- n-Heptane system using ultrasonic interferometer

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ABSTRACT

A study has been conducted on Acoustic Parameters of Heavy Fuel Oil- n-Heptane system. on different concentration's[1.0%,0.9%,0.8%,0.7% and 0.6%] at different temperature's of 30 °C, 35 °C, 40 °C, 45 °C and 50°C using Ultrasonic interferometer. Parameters like Ultrasonic velocity, Viscosity, Density, Adiabatic compressibility, Acoustic Impedance, Free length, Free Volume, Relation Time, Relative Association, Adsorption Coefficient and Molar compressibility are measured and helpful for correlation of Molecular interaction

Key words: Ultrasonic velocity, Viscosity, Density, Free Volume, Binary Mixture

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INTRODUCTION

Ultrasonic studies provide wealth information about the state of the liquid. Ultrasonic velocity measurement has been adequately employed to understand the nature of the molecular interaction in binary mixture [1- 6] and ionic interaction in electrolytic solution [7]. Measurement of ultrasonic velocity and other acoustical properties can be related to physico- chemical behavior and molecular interaction [8-15] in a number of binary systems. The investigations were carried out on the heavy fuel oil-n-Heptane system by ultrasonic method [16-18]. The ultrasonic studies on heavy fuel oil-n-Heptane system at 30 °C, 35 °C, 40 °C, 45 °C and 50°C. The acoustic parameters have been calculated for these two binary mixtures at different concentration of heavy fuel oil.

EXPERIMENTAL SECTION

Heavy fuel oil and n-Heptane (AR grade) are used. The heavy fuel oil was dissolved in the n-Heptane of various ratio's to prepare different concentration 1.0%,0.9%,0.8%,0.7%, and 0.6%.The binary mixture are prepared by using volume percentage(%) by using jobs variation method [19-21]. The ultrasonic velocity (U) have been measured using ultrasonic interferometer (Model F81) supplied by Mittal Enterprises, New Delhi operating frequency of 2 MHz with accuracy of $\pm$ 0.1%. The viscosities (ή) of pure compounds and their binary mixture were determined using Cannon Fensky viscometer by calibrating with double distilled water. The densities (ρ) of heavy fuel oil and h-heptane were measure accurately using 10ml specific gravity bottle in an electronic balance precisely and the accuracy in weighing is $\pm$ 0.1 mg. The temperature of the pure solution and the binary mixture were maintained at 30 °C, 35 °C, 40 °C, 45 °C and 50°C with $\pm$ 0.1°C accuracy using a thermostat. The acoustical parameters are calculated from U, ρ, and ή [22- 26] using following relation.

1. Adiabatic Compressibility (β)

The structural changes of the molecule in the mixture take place due to existence of electrostatic field between interacting molecules. The structural arrangement of molecules results in a considerable change in a adiabatic compressibility, which can be express as

$$\beta = 1/ U^2\rho \ Kg^{-1}ms^2$$

Where U is ultrasonic velocities and ρ is density of liquid mixtures.

2. Free Length (L_f)
The free length is the distance covered by sound wave between the surfaces of the neighbouring molecules and is related to ultrasonic velocity and density as

$Lf = K / (\rho U)^{1/2} m$, $K=(93.875 + 0.345T) \times 10^{-8}$

3. Acoustic Impedance (Z)
The specific acoustic impedance is related to density and ultrasonic velocity by the relation.

$Z=U\rho$ $Kgm^{-2}S^{-1}$

4. Relaxation Time (τ).
Relaxation time and adsorption coefficient are directly correlated. The adsorption of sound wave is the result of time lag between the passing of ultrasonic wave and return of molecular to their equilibrium position. It is computed using the relation

$\tau = 4\eta / 3 \rho U^2$ sec

5. Free Volume (V_f)
The free volume is defined as the average volume in which the centre of the molecule can move inside the hypothetical cell due to the repulsion of surrounding molecules. Free volume can be calculated by different and is given by

$(V_f) = [M_{eff} U / K \eta]^{3/2}$ m^3 mol^{-1}

Where K=4.28 X 10^9 M_{eff} = Effective molecular weight.

Effective molecular weight of liquid mixture is given by

$M_{eff} = X_1M_1 + X_2M_2$

Where X_1 and X_2 are the mole fraction of the first and second component and M1and M2 are molecular weights of the first and second component respectively.

6. Available Volume (V_a)
Available volume is the direct measure of compactness and strength of binding between the molecules of liquid or liquid mixture. Another parameter which can be calculate from ultrasonic velocity is the available volume and is given by

$V_a = V[1-U/U\infty]$ m^3 mol^{-1}

Where U∞ = Schaaf's limiting value taken as 1600m/s for liquids.

7. **Relative Association (Ra)**
Relative association can be calculated from density and ultrasonic velocity and is given by

$Ra = (\rho/\rho_o)^* (U/U_0)^{1/3}$

8. **Absorption coefficient (α/f^2)**
Absorption coefficient is also called attenuation coefficient is a characteristic parameter of medium and it depends on external condition like temperature, pressure and frequency of measurement is given by

$(\alpha/f^2) = 8\Pi^2\eta/[3\rho U^3]$.$Npm^{-1}s^2$

9. **Molar compressibility or Wada's constant (B)**
Molar compressibility is also known as Wada's constant, which is dependent on adiabatic compressibility and density, is given by

B = (M/ρ) k^{-17}

10.**Rao's constant or molar sound velocity (R)**
Rao's constant is also known as molar sound velocity and it is an additive property. It has been found to be invariant with temperature and pressure for unassociated organic and inorganic liquid. R is an relation between sound velocity and molar volume, which is given by

R = (Meff/ ρ) $U^{1/3}$

REUSLTS AND DISCUSSION

The measured Ultrasonic Velocity (U), Density (ρ) and Viscosity (η) with increase in concentration of heavy fuel oil with n-Heptane at five different temperatures is given in table-1to 3.

DENSITY

The Density of Heavy fuel oil-n-Heptane system increases with increases in concentration and decreases with increases temperature it is clearly visible is given table-1 and shown in fig:-1.

Table-1 Concentration and density values for the binary mixture of Heavy Fuel Oil –n-Heptane at 30 °C, 35 °C, 40 °C, 45 °C and 50°C

Concentration %	Density ρ/ kgm $^{-3}$				
	30 ^{0}C	35 ^{0}C	40 ^{0}C	45 ^{0}C	50 ^{0}C
1	648.8	642.9	639.6	636.4	633.1
0.9	648.6	647.8	641.5	638.3	635.0
0.8	648.0	645.3	642.1	638.8	635.6
0.7	646.1	641.9	638.7	635.4	632.1
0.6	645.2	644.8	642.3	639.1	635.8

ULTRASONIC VELOCITY

The ultrasonic velocity decreases with increases in the concentration of heavy fuel oil in n-Heptane system at 30 ^{o}C, 35 ^{o}C, 40 ^{o}C, 45 ^{o}C and 50^{o}C. This trend suggests that the dipole-dipole interaction is less at higher concentration of heavy fuel oil in the binary mixture. When the temperature is increased in heavy fuel oil-n-Heptane system, the ultrasonic velocity decreases is given in the table-2 and shown in fig:-2. This trend reveals that at higher temperature the molecular interaction between the components is low. The ultrasonic velocity of heavy fuel oil decreases and increases at some concentration shows a discrepancy, this is because of steric effect.

Table-2 Concentration and ultrasonic velocity values for the binary mixture of Heavy Fuel Oil –n-Heptane at 30 °C, 35 °C, 40 °C, 45 °C and 50°C

Concentration %	Ultrasonic Velocity U/ms $^{-1}$				
	30 ^{0}C	35 ^{0}C	40 ^{0}C	45 ^{0}C	50 ^{0}C
1	0.2644	0.2674	0.2547	0.2607	0.2529
0.9	0.2666	0.2683	0.2562	0.2517	0.2575
0.8	0.2762	0.2757	0.2655	0.2555	0.2532
0.7	0.2785	0.2756	0.2587	0.261	0.2442
0.6	0.2771	0.2684	0.2680	0.2608	0.2671

VISCOSITY

The Viscosity of Heavy fuel oil-n-Heptane system increases with increases in concentration and decreases with increases temperature it is clearly visible, since viscosity is temperature dependent is given in the table.-3 and shown in the fig:-3.

Table-3 Concentration and Viscosity values for the binary mixture of Heavy Fuel Oil –n-Heptane at 30 °C, 35 °C, 40 °C, 45 °C and 50°C

Concentration %	Viscosity η/10^{-4} Nsm $^{-2}$				
	30 ^{0}C	35 ^{0}C	40 ^{0}C	45 ^{0}C	50 ^{0}C
1	0.3135	0.2764	0.2811	0.3724	0.4811
0.9	0.2944	0.2874	0.2948	0.3852	0.5036
0.8	0.2868	0.2796	0.2790	0.3728	0.4933
0.7	0.2864	0.2758	0.2796	0.3718	0.4808
0.6	0.2863	0.2694	0.2750	0.3731	0.4819

The acoustic parameters for various composition of Heavy fuel oil with n-Heptane sysytem at various tempersture 30 ^{o}C, 35 ^{o}C, 40 ^{o}C, 45 ^{o}C and 50^{o}C are calculated from measure ultrasonic velocity, density and viscosity. These data's are given in the table 4to14.

ADIABATIC COMPRESSIBILITY(β)

The plots of adiabatic compressibility against concentration of Heavy fuel oil-n-Heptane binary mixture at 30 ^{o}C, 35 ^{o}C, 40 ^{o}C, 45 ^{o}C and 50^{o}C are given in table -4 and shown in the figure :-4

According to Forte and Moore [27] hydrogen bonding between unlike component makes a negative contribution to compressibility. It may be noted that in the five different temperature, the β values increases with increases in concentration of the entire component indicating the option of weaker interaction at higher concentration. It is also observed that the interactions are less at lower temperature at specific concentration.

The adiabatic compressibility values increases with increase in the concentration of heavy fuel oil in all the five different temperatures. This trends shows that the molecular attraction more at lower concentration of heavy fuel oil and at higher concentration the attraction are less due to steric hindrance and dipole-dipole interaction are more at higher temperature than at lower temperature. At 0.7% concentration the variation occurs because of less steric and dipole-dipole interaction. The plot of concentration versus adiabatic compressibility is given in the table-4 and shown in fig:-4

Table-4 Concentration and Adiabatic compressibility values for the binary mixture of Heavy Fuel Oil –n-Heptane at 30 ^{o}C, 35 ^{o}C, 40 ^{o}C, 45 ^{o}C and 50^{o}C

Concentration %	Adiabatic compressibility/10^{3} kg-1 ms^{-2}				
	30 ^{0}C	35 ^{0}C	40 ^{0}C	45 ^{0}C	50 ^{0}C
1	0.02205	0.02175	0.02410	0.02312	0.02469
0.9	0.02175	0.02144	0.02375	0.02473	0.02375
0.8	0.02021	0.02038	0.02213	0.02398	0.02416
0.7	0.01995	0.02051	0.02351	0.02310	0.02653
0.6	0.02018	0.02153	0.02168	0.02300	0.02221

ACOUSTIC IMPENDANCE (Z)

Acoustic Impedance increases and decreases in Heavy fuel oil system at specific temperature investigated. The increases and decreases in acoustic impedance can be explained on the basis of lyophobic interaction between solute and solvent molecule [28, 29]. The plots of acoustic impedance versus concentration of heavy fuel oil –n-Heptane sysytem are given in fig 5 and shown in the fig:-4.

Table-5 Concentration and Acoustic Impedance values for the binary mixture of Heavy Fuel Oil –n-Heptane at 30 ^{o}C, 35 ^{o}C, 40 ^{o}C, 45 ^{o}C and 50^{o}C

Concentration %	Acoustic impedance Z/$10^{-3}$$kgm^{-2}s^{-1}$				
	30 ^{0}C	35 ^{0}C	40 ^{0}C	45 ^{0}C	50 ^{0}C
1	171.543	171.911	162.906	165.909	160.111
0.9	172.917	173.804	164.352	160.660	163.512
0.8	178.978	177.909	170.478	163.213	163.466
0.7	179.939	176.908	165.232	165.772	165.539
0.6	178.785	173.064	172.136	166.677	169.822

FREE LENGTH

The free length of a system is measure of intermolecular attraction between the components in binary mixuters. This increase and decreases in free length indicates weaking and strengthing of intermolecular attraction. As the ultrasonic velocity increases due to the increases in concentration, the interaction free length has to decrease and vice-versa [30].

The free length values increases with increase in concentration of heavy fuel oil-n-Heptane system at different temperature which shows that the dipole-dipole interaction are less at higher concentration in all the system. The plot of concentraton versus free length given in the table-6 and shown in fig:-6.

Table-6 Concentration and Free Length values for the binary mixture of Heavy Fuel Oil –n-Heptane at 30 ^{o}C, 35 ^{o}C, 40 ^{o}C, 45 ^{o}C and 50^{o}C

Concentration %	Free length L_f				
	30 ^{0}C	35 ^{0}C	40 ^{0}C	45 ^{0}C	50 ^{0}C
1	29.4732	29.5258	30.1971	30.9634	32.2326
0.9	29.2300	29.3153	31.2223	32.0227	31.6487
0.8	28.2271	28.8236	30.1146	31.5342	31.9208
0.7	28.0351	28.6696	30.9884	30.9521	33.4488
0.6	28.1964	29.3725	29.8290	30.8861	30.4919

MOLAR COMPRESSIBILITY OR WADA'S CONSTANT

The molar compressibility of heavy fuel oil with n-Heptane system decreases with increase in concentration and increases with temperature is given in the table-7 and shown in the fig:-7.

Table-7 Concentration and molar compressibility values for the binary mixture of Heavy Fuel Oil –n-Heptane at 30 ºC, 35 ºC, 40 ºC, 45 ºC and 50ºC

Concentration %	Molar compressibility(B) 10^{-11}				
	30 ^{0}C	35 ^{0}C	40 ^{0}C	45 ^{0}C	50 ^{0}C
1	2.8906	2.9177	2.9328	2.9475	2.9629
0.9	2.8915	2.8957	2.9241	2.9387	2.9540
0.8	2.8941	2.9069	2.9214	2.9364	2.9551
0.7	2.9026	2.9223	2.9369	2.9522	2.9675
0.6	2.9067	2.9091	2.9204	2.9351	2.9503

FREE VOLUME (V_f)

Table- 8 Contain Free volume values for concentration of different temperature of Heavy fuel oil-n-Heptane system. The trends present in heavy fuel oil-n-heptane system are that free volume decreases with increases in concentration, increases and then decrease with increases in temperature is given in the table :-8 and shown in the fig:-8.

Table-8 Concentration and Free Volume values for the binary mixture of Heavy Fuel Oil-n-Heptane at 30 ºC, 35 ºC, 40 ºC, 45 ºC and 50ºC

Concentration %	Free Volume V_f /10^{-24} m^3				
	30 ^{0}C	35 ^{0}C	40 ^{0}C	45 ^{0}C	50 ^{0}C
1	3.921	5.918	4.862	2.242	0.949
0.9	4.057	5.299	4.275	1.817	0.871
0.8	4.048	6.236	5.581	2.093	1.142
0.7	4.549	6.474	5.140	2.119	0.850
0.6	4.181	6.401	5.991	2.103	1.102

RAO'S CONSTANT

Table-9 contains Rao's constant values for concentration of different temperature of Heavy fuel oil-n-Heptane system. The concentration and Rao's constant values for the binary mixture of Heavy Fuel Oil –n-Heptane at 30 ^{o}C, 35 ^{o}C, 40 ^{o}C, 45 ^{o}C and 50^{o}C shown in Fig:-9

Table-9

Concentration %	Rao's Constant				
	30 ^{0}C	35 ^{0}C	40 ^{0}C	45 ^{0}C	50 ^{0}C
1	0.013695	0.013977	0.013383	0.014099	0.013424
0.9	0.013798	0.013903	0.013406	0.013237	0.013612
0.8	0.014302	0.014335	0.013874	0.013467	0.013159
0.7	0.014451	0.014390	0.013579	0.013771	0.012952
0.6	0.014387	0.013943	0.013977	0.013669	0.014073

AVAILABLE VOLUME

Table- 10 contains available Volume values for Concentration of different temperature and Available Volume values for the binary mixture of Heavy Fuel Oil –n-Heptane at 30 ^{o}C, 35 ^{o}C, 40 ^{o}C, 45 ^{o}C and 50^{o}C shown in fig:-10.

Table-10

Concentration %	Available Volume V_a m^3				
	30 ^{0}C	35 ^{0}C	40 ^{0}C	45 ^{0}C	50 ^{0}C
1	0.15600	0.15689	0.15760	0.15840	0.15922
0.9	0.15519	0.15543	0.15696	0.15775	0.15857
0.8	0.15517	0.15517	0.15674	0.15755	0.15889
0.7	0.15519	0.15666	0.15745	0.15826	0.15909
0.6	0.15486	0.15582	0.15643	0.15722	0.15803

RELAXATION TIME

Table- 11 contains the Relaxation time values for concentration of different temperature and Relaxation time values for the binary mixture of Heavy Fuel Oil –n-Heptane at 30 ^{o}C, 35 ^{o}C, 40 ^{o}C, 45 ^{o}C and 50^{o}C is shown in fig:-11.

Table-11

Concentration %	Relaxation time $\tau/10^{-3}$ s				
	30 ^{0}C	35 ^{0}C	40 ^{0}C	45 ^{0}C	50 ^{0}C
1	9.216	8.0170	9.0330	11.4798	15.8417
0.9	9.067	8.2176	9.4489	12.7008	15.9476
0.8	8.456	7.6005	8.2189	11.9198	15.8913
0.7	8.342	7.5643	8.7214	11.4530	16.9963
0.6	8.437	7.7329	7.9481	11.4441	14.1624

MOLAR VOLUME

Table- 12 contains the molar volume values for concentration of different temperature and Molar Volume values for the binary mixture of Heavy Fuel Oil –n-Heptane at 30 ^{o}C, 35 ^{o}C, 40 ^{o}C, 45 ^{o}C and 50^{o}C is shown in the fig:-12

Table-12

Concentration %	Molar Volume V_m				
	30 ^{0}C	35 ^{0}C	40 ^{0}C	45 ^{0}C	50 ^{0}C
1	0.15539	0.15682	0.15760	0.15842	0.15925
0.9	0.15527	0.15478	0.15630	0.15699	0.15781
0.8	0.15534	0.15599	0.15677	0.15758	0.15892
0.7	0.15567	0.15668	0.15760	0.15829	0.15912
0.6	0.15576	0.15585	0.15646	0.15720	0.15806

RELATIVE ASSOCIATION.

Table- 13 contains the relative Association values for concentration of different temperature and Relative Association values for the binary mixture of Heavy Fuel Oil –n-Heptane at 30 ^{o}C, 35 ^{o}C, 40 ^{o}C, 45 ^{o}C and 50^{o}C is shown in fig:-13.

Table-13

Concentration %	Relative Association R_a				
	30 ^{0}C	35 ^{0}C	40 ^{0}C	45 ^{0}C	50 ^{0}C
1	3.4190	3.2062	3.3345	3.2021	3.0407
0.9	3.4007	3.2198	3.3249	3.3265	3.0700
0.8	3.2749	3.1212	3.2114	3.2796	3.1742
0.7	3.2412	3.1036	3.2784	3.1934	3.2224
0.6	3.2646	3.2037	3.1824	3.2145	2.9633

ADSORPTION COEFFICIENT

Table- 14 contains Adsorption coefficient values for concentration of different temperature and Absorption Coefficient values for the binary mixture of Heavy Fuel Oil –n-Heptane at 30 ^{o}C, 35 ^{o}C, 40 ^{o}C, 45 ^{o}C and 50^{o}C is shown in the fig:-14.

Table-14

Concentration %	Absorption coefficient $\alpha/f2\ 10^{-14}$Npm-1s^2				
	30 ^{0}C	35 ^{0}C	40 ^{0}C	45 ^{0}C	50 ^{0}C
1	0.68734	0.59122	0.69937	0.86835	1.23525
0.9	0.67067	0.60398	0.71851	0.99506	1.22130
0.8	0.60369	0.54363	0.61045	0.91998	1.23765
0.7	0.59060	0.53967	0.66480	0.86533	1.37335
0.6	0.60043	0.56815	0.58483	0.86531	1.04582

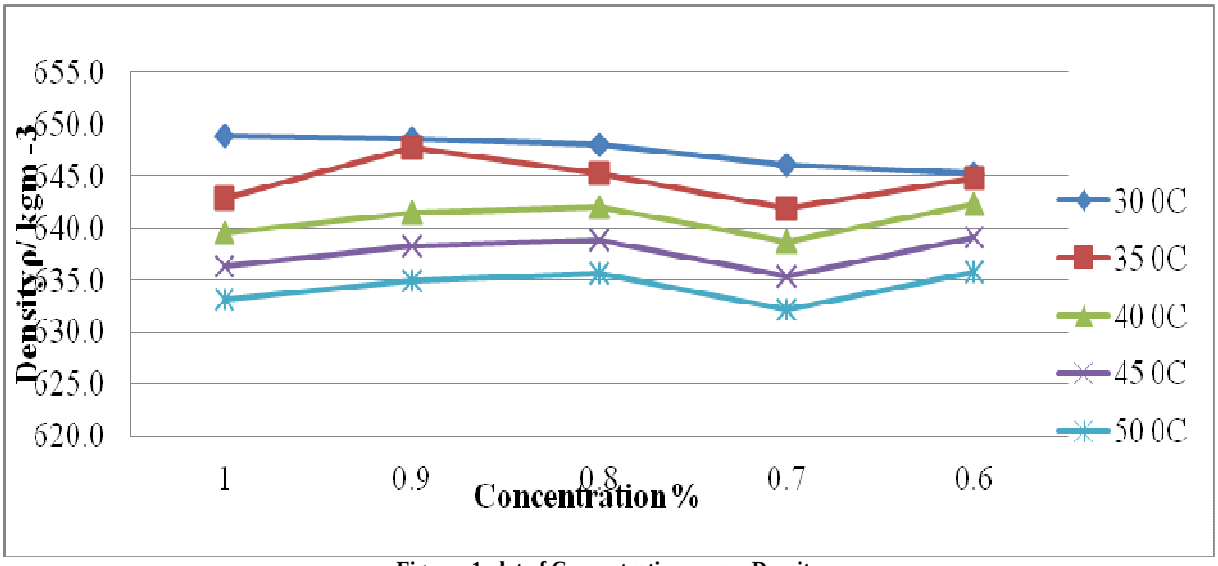

Figure:-1 plot of Concentration versus Density

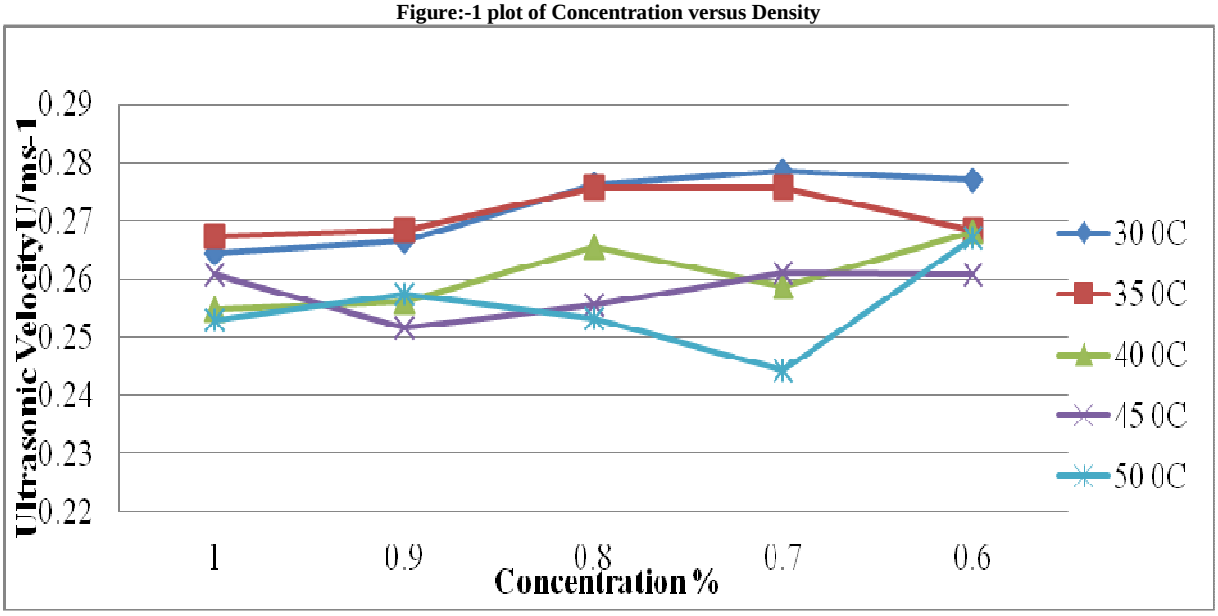

Figure:2 plot of concentration versus Ultrasonic Velocity

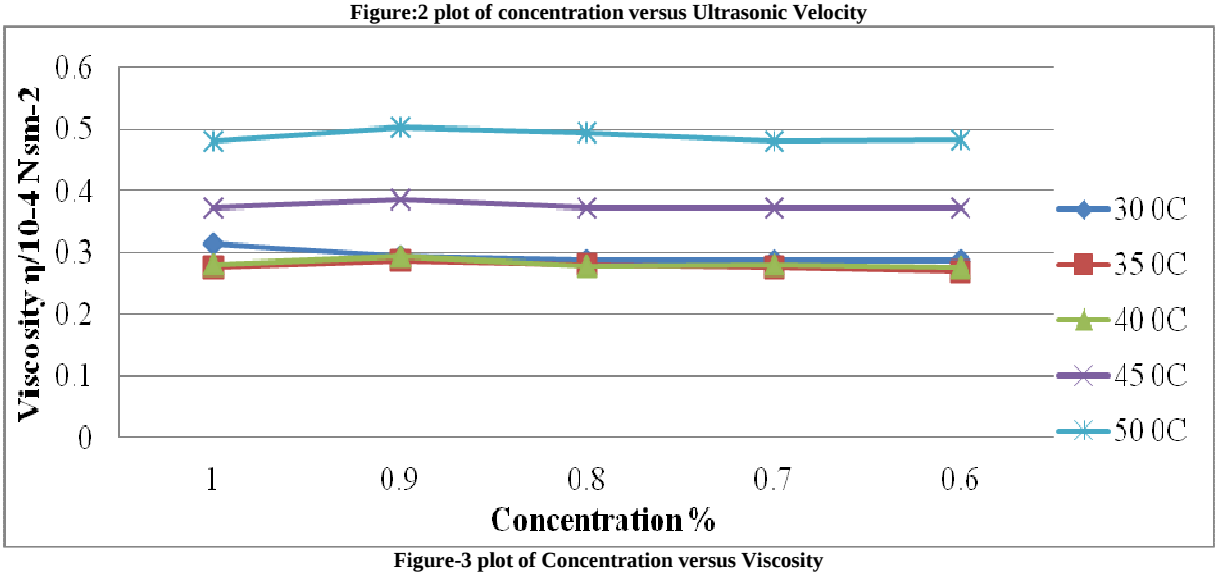

Figure-3 plot of Concentration versus Viscosity

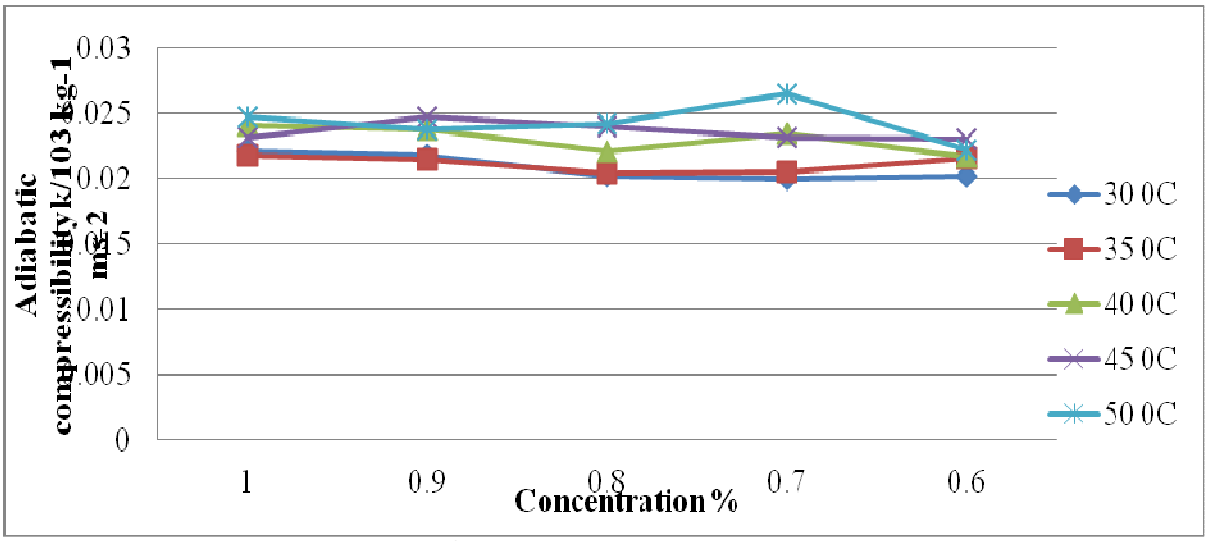

Figure-4 plot of concentration versus Adiabatic compressibility

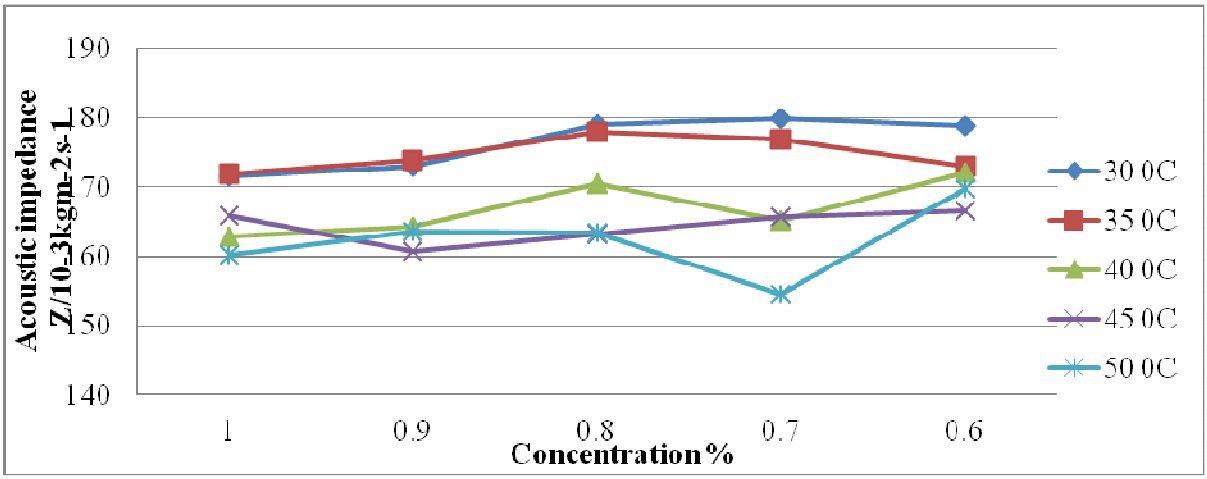

Fig:5 Plot of concentration versus Acoustic Impedance

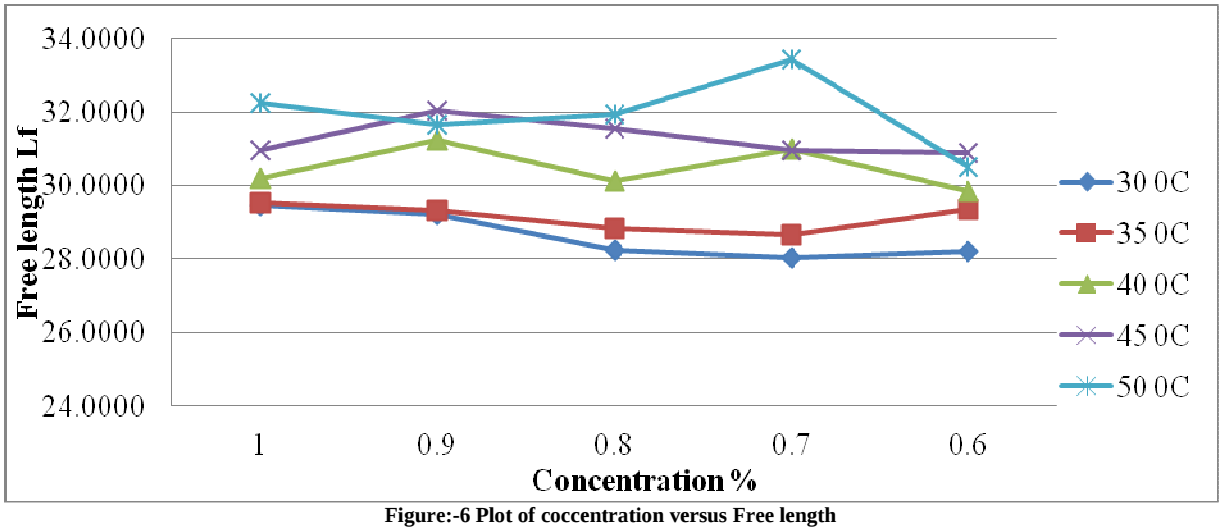

Figure:-6 Plot of coccentration versus Free length

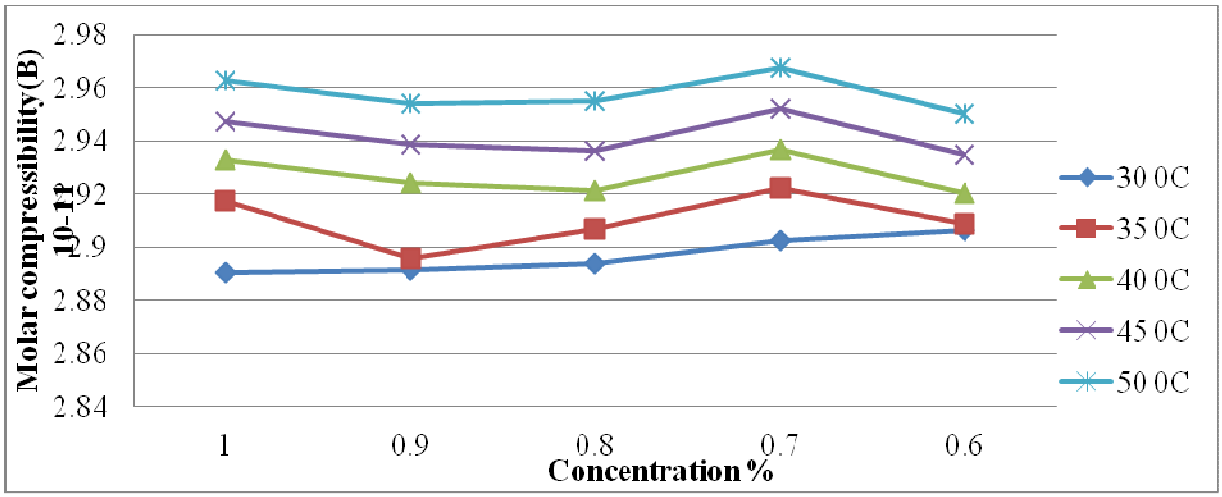

Figure:-7 Plot of concentration Versus Molar compressibility

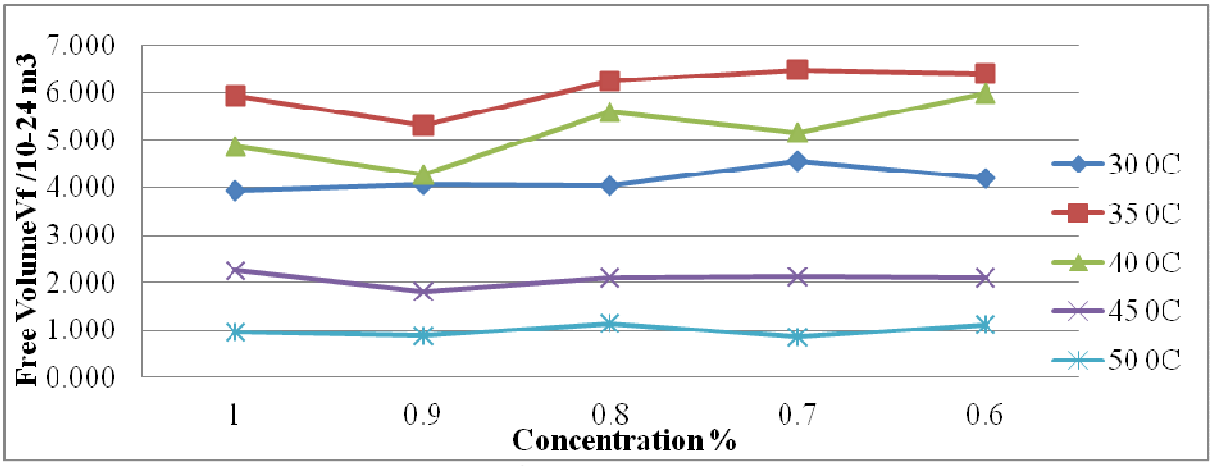

Figure:-8 plot of concentration versus Free volume

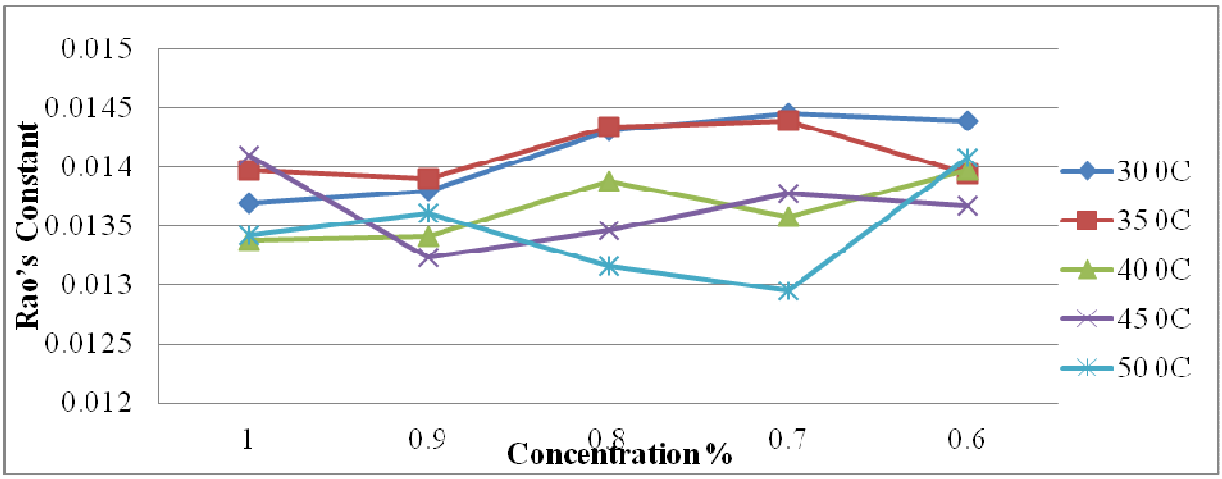

Figure:-9 plot of concentration versus Rao's constant

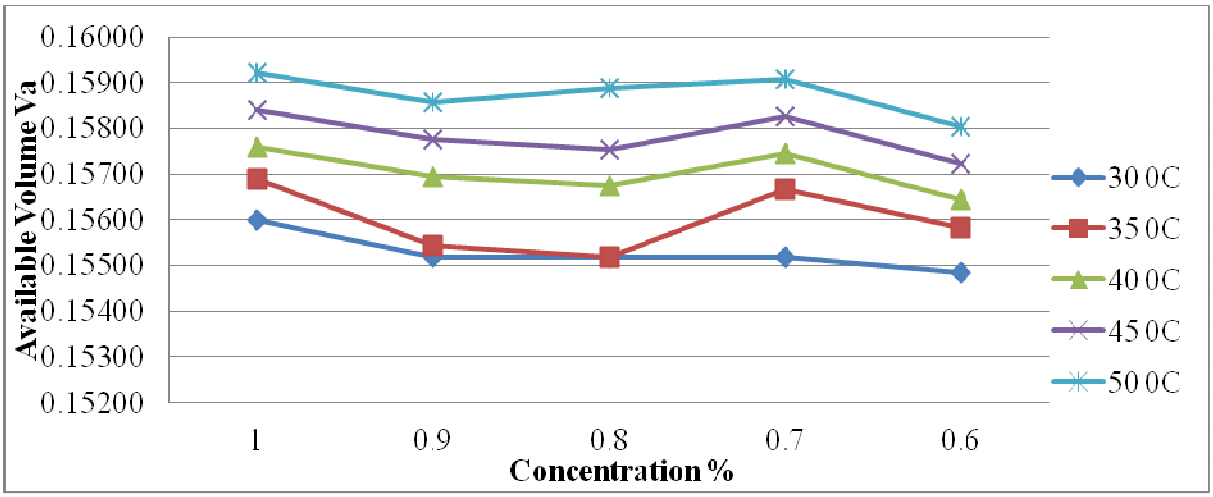

Figure:-10 plot of concentration versus available volume

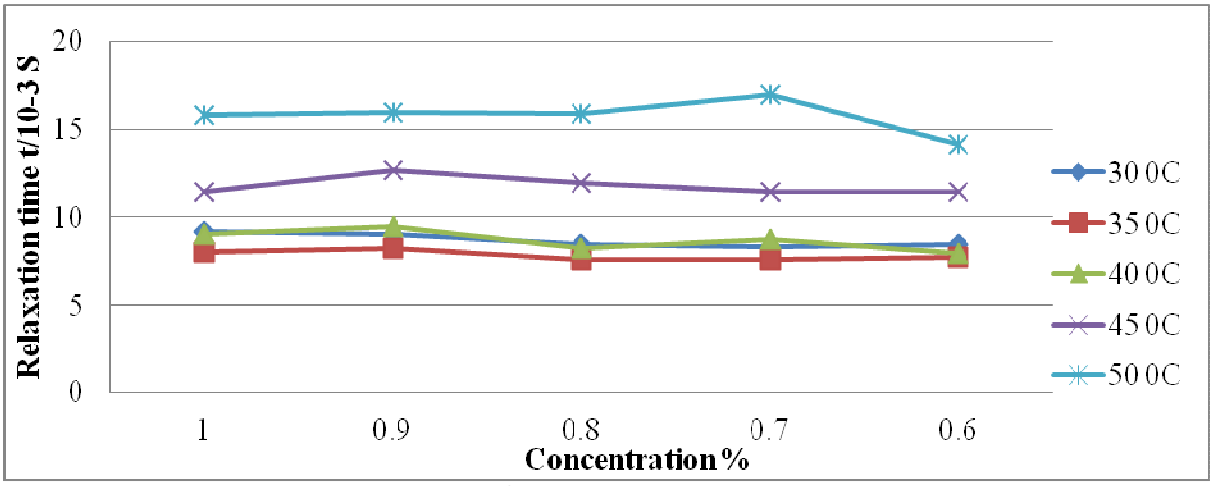

Figure:-11 plot of Concentration versus Relaxation time

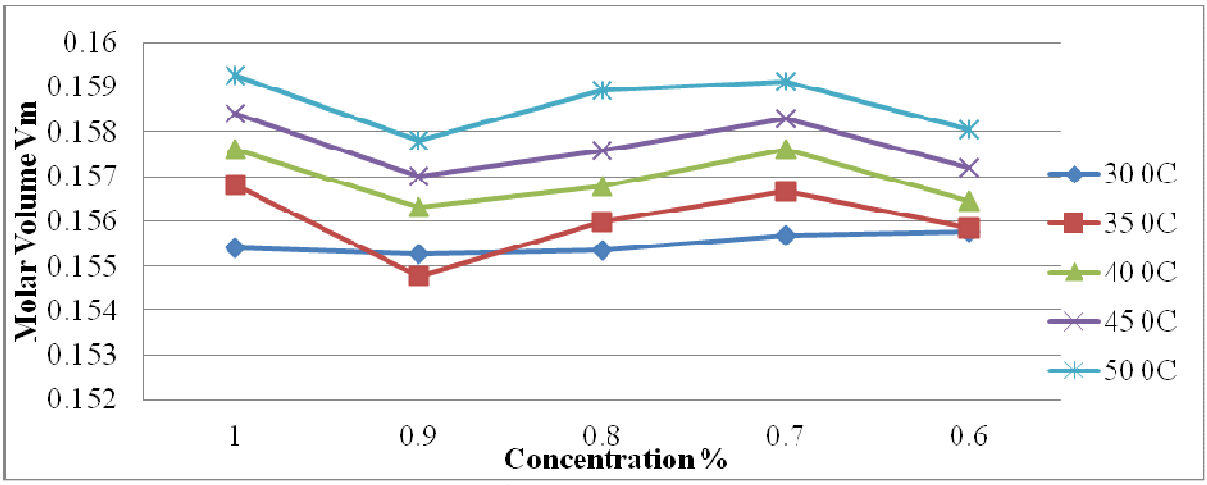

Figure:12 plot of Concentration versus Molar Volume.

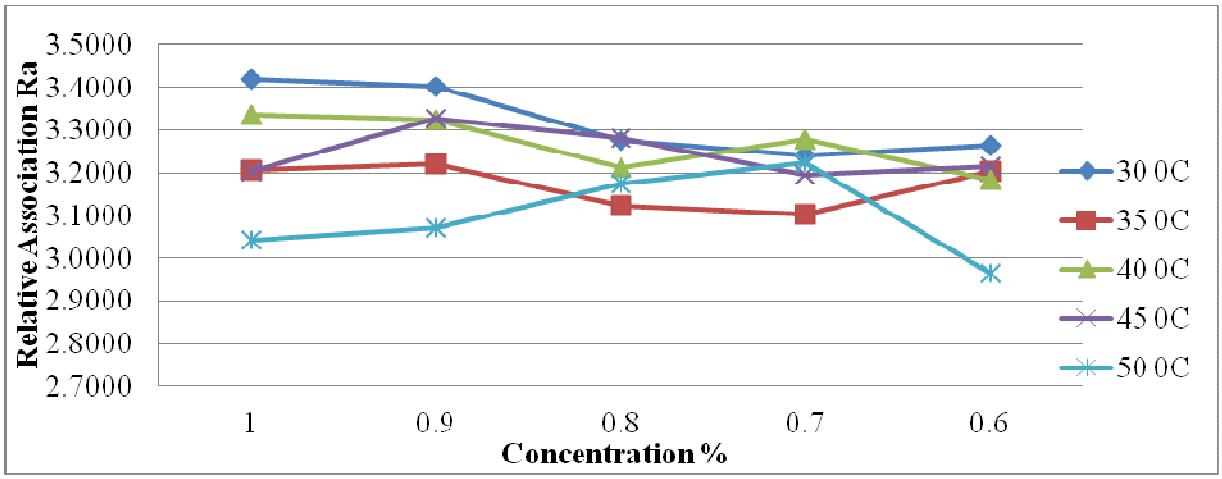

Figure:13 plot of Concentration versus Relative association.

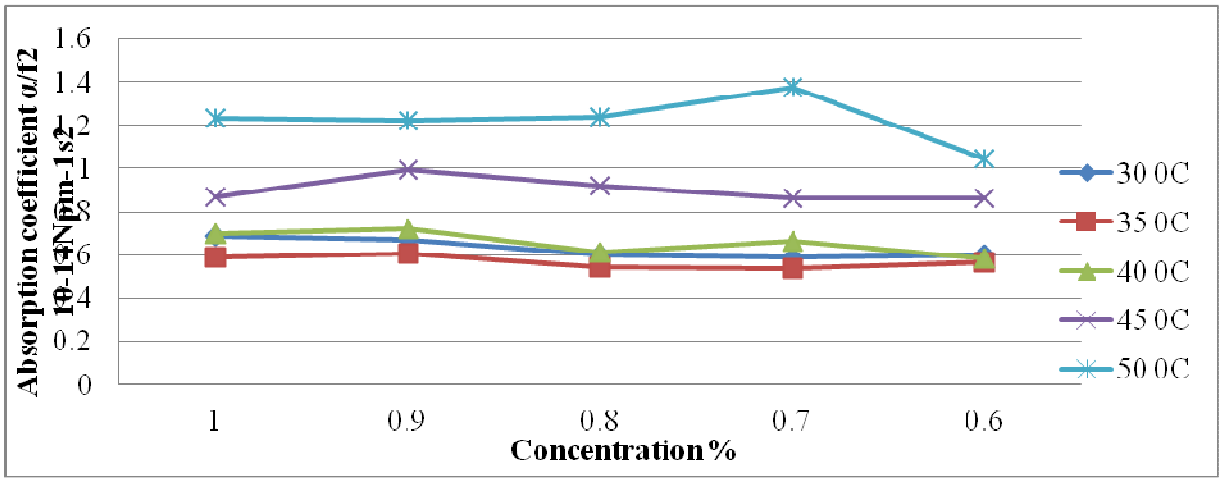

Figure:14 plot of concentration versus Adsorption coefficient.

CONCLUSION

In the present study, it can be inferred that there are interaction among the component of binary mixture. Leading to the possible hydrogen bond formation of type H-H between two component of each binary system. The molecular attraction increases in the concentration of heavy fuel oil n-heptane system investigated. But the molecular interaction decreases with increases in concentraction of heavy fuel oil n-heptane system due to steric hindrance. When the temperation increases increases, the interaction between the component decreases.

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