International Journal of Science and Research (IJSR)
ISSN: 2319-7064
Impact Factor 2024: 7.101

Study of Molecular Interactions in Binary Mixtures of Methyl Propyl Ketone and Methanol using Thermo-Acoustic Parameters at Different Temperatures

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Abstract: ***The Density (ρ), refractive index (nD), viscosity (η) and ultrasonic velocity (U) of pure components Methyl Propyl Ketone (MPK), Methanol (MA) and their binary liquid mixtures, have been determined as functions of composition at different temperatures (T=303.15 K,313.15 K, and 323.15 K) at a fixed frequency of 2 MHz over a different concentration ranges. The values of adiabatic compressibility (β_{ab}), intermolecular free length (L_f), acoustic impedance (Z), free volume (V_f), relaxation time (τ), were computed using experimental data at different temperature. The observed behaviour of these parameters concerning different compositions have been discussed in terms of their molecular interactions between the unlike molecules of the binary mixtures. Also the thermodynamic parameters such as Gibb's free energy (G), Wada's constant (W) Rao's constant (R) and various excess parameters calculated. The variation in these parameters have been discussed in terms of nature and strength of molecular interactions at varying temperature with composition of liquid mixtures.***

Keywords: Ultrasonic velocity, acoustic parameters, excess parameters

1. Introduction

Density, speeds of sound, refractive indices as a function of temperature, composition and their derivatives exhibits some insight in the molecular structure of liquid and provides information for intermolecular interactions to offer the quantitative background information For liquid mixtures needed for developing new technology process helps us to understand their real behavior and develop the models for their description as well as simulation process. Comprehensive of thermo physical properties of liquid mixtures containing the constituents associated through hydrogen bonds is important from theoretical and process design aspects because these properties strongly belongs on the hydrogen bonding strength of hydroxyl group chain length and on theoretical level, volumetric properties of these mixtures are essential sources of data for the characterization of the interactions between the constituents and useful for knowledge of liquid state theory[1-2]. Keeping these important aspects in mind, the present study deals with the ultrasonic and thermodynamic study of Methyl Propyl Ketone (MPK), Methanol (MA) over the entire mole fraction and temperature range (*T*=303.15 K,313.15 K, and 323.15 K). The liquids under investigation have been chosen based on their multifold applications. Ultrasonic velocities, densities and viscosities of the studied binary mixtures are measured and using the experimental data, excess molar volume, deviation in adiabatic compressibility, excess inter-molecular free length and deviation in viscosity are reported in this paper. The results have been used to estimate the molecular interactions in the constituent molecules.

2. Experimental Details

Methanol and Methyl Propyl Ketone (MPK) used were of AR grade with minimum assay of 99.9% procured form S.D. fine chemicals and Spectrochem Pvt. Ltd. Mumbai. These chemicals are used without further purification. Samples of solution with different mole fraction Methyl Propyl Ketone (MPK) were prepared. The density (ρ), viscosity (η) and refractive index (nD) of pure liquids and liquid mixtures were determined by using 10 ml Specific gravity bottle, Ostwald's viscometer AND Abbe's refractometer using Sodium D light respectively at temperatures range (*T*=303.15 K, 313.15 K, and 323.15 K). The Ultrasonic velocity (U) in the liquid and liquids mixtures have been measured using an Ultrasonic Fixed-frequency interferometer (Mittal type Model F-05)[3]. The interferometer is fixed frequency (2MHz). The measuring cell of the interferometer is a specially designed double walled vessel with provision to circulate water at various constant temperature (*T*=303.15 K, 313.15 K, and 323.15 K). The high frequency generator excites a quartz crystal fixed at the bottom of the vessel, at its resonant frequency. A fine micrometer screw at the top of the cell is used to raise or lower the reflector plate in the liquid through a known distance. The measuring cell is connected to the output terminals of the high frequency generator through a cable. Ultrasonic waves normal to quartz crystal are reflected from the reflector plate. Stationary waves are formed in the

region between reflector plate and the quartz crystal. The micrometer is slowly moved till a number of maximum readings (N) of the anode current is passed. The total distance (d) moved by the micrometer is noted. The velocity of ultrasonic waves in the binary liquid mixture was determined using the relation. $U = \lambda f$ Where $\lambda = 2d/N$ = wavelength of the ultrasonic waves in the binary liquid mixture and f is the frequency of the generator .The experimental values of density (ρ), viscosity (η) and ultrasonic velocity (U) were used to calculate various acoustical parameters such as adiabatic compressibility (β_{ad}), Acoustical impedance (Z), free length (L_f), relaxation time (τ) Rao's constant (R),Wada's constant (W) and Gibb's free energy using following expressions [3, 5]

$$\beta_a = \frac{U^2}{\rho} \quad \text{(i)}$$

$$Z = U\rho \quad \text{(ii)}$$

$$L_f = K_T \beta_a^{1/2} \quad \text{(iii)}$$

$$\tau = \frac{4}{3}\eta\,\beta_a \quad \text{(iv)}$$

$$W = \frac{\beta^{-1/7 \times M_{eff}}}{\rho} \quad \text{(v)}$$

$$R = \frac{U^{1/3 \times M_{eff}}}{\rho} \quad \text{(vi)}$$

$$\Delta G = K_B T\, 2.303\, log_{10}\left(\frac{K_B T \tau}{h}\right) \quad \text{(vii)}$$

Where, K_T is temperature dependent constant having value of 199.53×10^{-8} in MKS system and K is temperature dependent constant whose value is 4.28×10^9 in MKS system

$M_{eff} = \sum X_i M_i$ Where X is mole fraction and M is molecular weight in of i^{th} components

The strength of interaction between the component molecules is well reflected in the deviations, in excess viscosity (Δη) Excess Adiabatic compressibility ($\Delta\beta_{ad}$), Excess Acoustic impedance (ΔZ), Excess intermolecular free length (ΔL_f) excess free volume (ΔV_f) etc. These parameters were calculated using the relation.

$$\Delta Y = Y_m - (X_1Y_1 + X_2Y_2) \quad \text{(ix)}$$

Where, ΔY is any excess parameter, and Y refers to above mentioned parameter. The subscripts m, 1 and 2 used in the above equation are respectively for the mixture, component 1 and component 2, X_1 and X_2 are the mole fractions of two components in the liquid mixture.

3. Result and Discussion

The experimental values of density (ρ), viscosity (η) and ultrasonic velocity (U) were used to calculate various acoustical parameters such as adiabatic compressibility (β_{ad}), Acoustical impedance (Z), free length (L_f),free volume (V_f) ,relaxation time (τ) for Methanol, Methanol and Methyl Propyl Ketone (MPK) and their binary mixtures at various constant temperature (T=303.15 K, 313.15 K, and 323.15 K). are listed in table (1)

Ultrasonic velocity of sound waves in a medium is fundamentally related to the binding forces between the molecules. From fig. (1), it is observed that ultrasonic velocity (U) increases with mole fraction of MPK and decreases with increase of temperature The increase in ultrasonic velocity with mole fraction of MPK indicates the changes in the compressibility and elastic properties of mixture it may be due to molecular association in the binary mixture[9] velocity decreases with rise in temperature it is because the system reduces molecular connections due to thermal agitation and weakened intermolecular forces similar results were reported by other researchers[15-17]

The variation in the values of intermolecular free length L_f mole fraction of MPK at various temperature are shown in fi.2. Intermolecular free length changes significantly due to molecular interactions influencing sound velocity and compressibility between components. A rise in temperature results in an increase in free length due to the thermal expansion of liquids.[2]

The variation in the values of adiabatic compressibility with mole fraction of MPK at various temperature indicate that the free dipoles of methanol molecules would induced moments in the neighbouring molecules of the MPK, resulting in dipolar induced dipolar interaction leading to contraction in the volume This leads to subsequent variation in the adiabatic compressibility (β_{ad}) as well as intermolecular free length (L_f)[12].

The values of Gibbs free energy, Wada's constant and Rao's constant with mole fraction of MPK at various temperature are shown in table2. Wada's constant and Rao's constant are linked with the molecular compressibility providing important insight into the molecular interactions within the liquid mixture. From table 2 it is found that both Wada's constant and Rao's constant increases with mole fraction of MPK in the mixture suggest the stronger solute –solute molecular interaction leading to closer structure formation[18].

The excess parameters of a binary liquid system is a measure of deviation from the ideal behaviour of the mixture and are more sensitive towards the molecular interactions in the liquid mixture

The respective excess parameters have been calculated and plots are drawn in figures 4 to 6 The molecular packing of the systems determines a quantity called specific acoustic impedance [19]. The sign and magnitude of excess acoustic impedance provide valuable insights into the nature of molecular interactions. The Positive excess acoustic impedance values (.Fig 5) suggest strong interactions. The relaxation time reflect the time taken for excitation energy to translate into molecular motion and provides insight into relaxation process. Variation of excess relaxation time with mole fraction of MPK is illustrated in fig.6.The negative deviation of these values indicates formation of molecular association between unlike molecules. Thus the strong interaction existing between the components were confirmed.

4. Conclusion

1) Acoustic parameters in Methanol and MPK system suggest strong molecular interaction in unlike molecules of system.
2) Non-linear behavior of excess acoustic and thermodynamic parameters suggest the formation of molecular association in the binary mixtures

Table 1

The values of density (ρ), viscosity(η), Refractive Index(nD) ultrasonic velocity (U), adiabatic compressibility (β_{ad}), intermolecular free length (L_f), Acoustic impedance (Z) , and relaxation times (τ) of the binary liquid mixture of methanol+ MPK with mole fraction (X_{MPK}) of MPK at various constant temperature (*T*=303.15 K, 313.15 K, and 323.15 K).

At temperature *T*=303.15 K								
X_{MPK}	ρ (kg/m3)	η (x10^{-3}Pa.s)	nD	U (m/s)	βad (X10-10)m/N	Z (kg/m^{2}s)	L_F (x 10^{-11} m)	τ (x10^{-13}) sec
0.000	782.88	0.552	1.325	1077.6	11.00	843631	6.5805	8.1027
0.040	784.06	0.541	1.332	1086	10.81	851489	6.5247	8.0616
0.086	786.12	0.521	1.340	1112.8	10.27	874794	6.3592	7.5137
0.139	788.46	0.504	1.346	1121	10.09	883864	6.3033	6.7770
0.200	788.86	0.515	1.353	1129.6	9.93	891096	6.2537	6.8258
0.273	791.56	0.508	1.358	1141.2	9.70	903328	6.1796	6.5761
0.361	792.59	0.503	1.364	1150.8	9.52	912113	6.1241	6.3907
0.467	795.42	0.495	1.370	1164	9.27	925869	6.0438	6.1262
0.601	798.26	0.502	1.375	1177.2	9.03	939712	5.9654	6.0564
0.772	799.41	0.495	1.381	1186	8.89	948100	5.9169	5.8676
1.000	801.68	0.515	1.386	1190.4	8.80	954320	5.8867	6.0484

At temperature *T*=313.15 K								
X_{MPK}	ρ (kg/m3)	η (x10^{-3}Pa.s)	nD	U (m/s)	βad (X10-10)m/N	Z (kg/m^{2}s)	L_F (x 10^{-11} m)	τ (x10^{-13}) sec
0.000	773.73	0.463	1.321	1052.8	11.66	814583	6.8930	7.2000
0.040	778.28	0.461	1.327	1068	11.26	831203	6.7750	6.9566
0.086	780.79	0.453	1.336	1077	11.04	840911	6.7076	6.6631
0.139	781.42	0.436	1.342	1089.2	10.78	851123	6.6298	6.2675
0.200	783.71	0.436	1.349	1100.8	10.53	862708	6.5503	6.1259
0.273	784.04	0.439	1.354	1105.2	10.44	866521	6.5229	6.1185
0.361	785.82	0.439	1.360	1113.6	10.26	875089	6.4664	6.0116
0.467	787.02	0.420	1.365	1126	10.02	886185	6.3903	5.6081
0.601	788.22	0.422	1.371	1134	9.865	893841	6.3404	5.5515
0.772	789.23	0.407	1.376	1142	9.715	901301	6.2919	5.2725
1.000	791.4	0.442	1.381	1158	9.422	916441	6.1965	5.5563

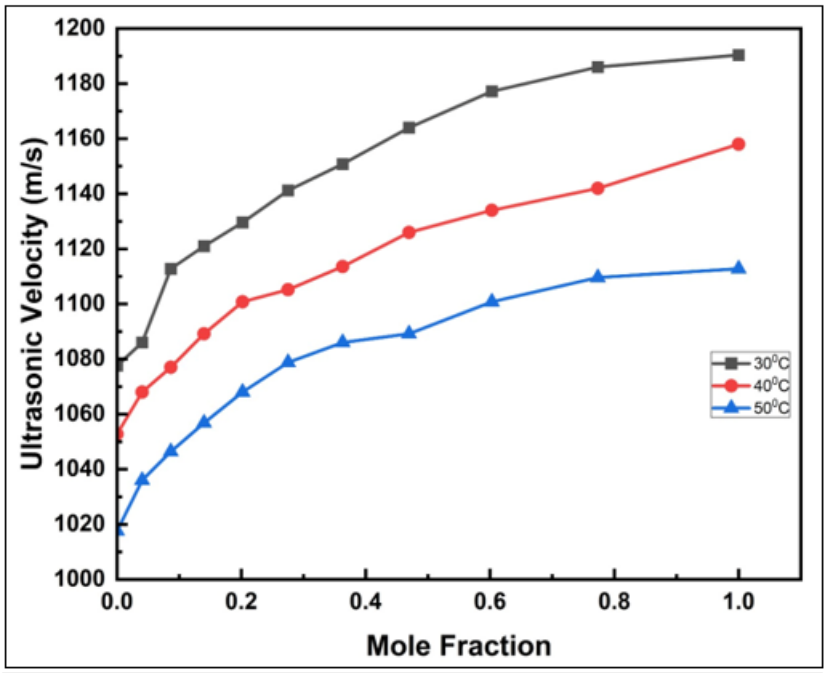
At temperature *T*=323.15 K								
X_{MPK}	ρ (kg/m3)	η (x10^{-3}Pa.s)	nD	U (m/s)	βad (X10-10)m/N	Z (kg/m^{2}s)	L_F (x 10^{-11} m)	τ (x10^{-13}) sec
0.000	756.09	0.3916	1.317	1017.6	12.77	769397	7.3374	6.6695
0.040	758.64	0.3917	1.323	1036	12.28	785951	7.1950	6.4147
0.086	761.02	0.3797	1.332	1046.4	12.00	796331	7.1123	6.0763
0.139	762.12	0.3757	1.338	1056.8	11.75	805408	7.0372	5.8848
0.200	764	0.3793	1.345	1068	11.48	815952	6.9549	5.8028
0.273	766.11	0.3672	1.350	1078.8	11.22	826479	6.8758	5.4917
0.361	768.04	0.3599	1.356	1086	11.04	834091	6.8216	5.2982
0.467	770.11	0.3481	1.361	1089.2	10.95	838804	6.7924	5.0797
0.601	773.86	0.3648	1.367	1100.8	10.66	851865	6.7045	5.1872
0.772	776.02	0.3595	1.371	1109.6	10.47	861072	6.6421	5.0165
1.000	778	0.3612	1.376	1112.8	10.38	865758	7.3374	4.9993

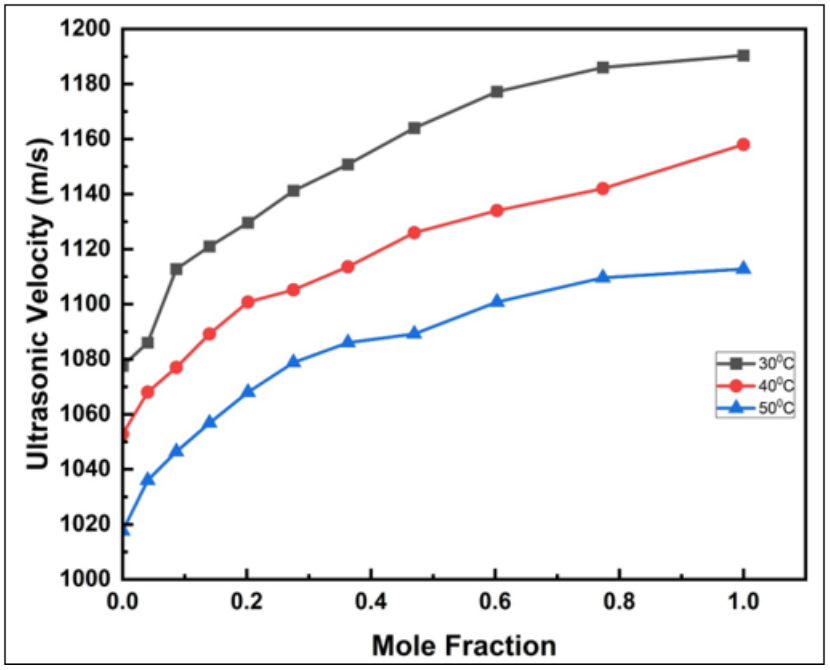
Table 2

The values of Gibbs free energy(ΔG), Wada's constant (W) and Rao's constant for binary mixtures of Methanol+ MPK) of the binary liquid mixture of methanol+ MPK with mole fraction (X_{MPK}) of MPK at various constant temperature (*T*=303.15 K, 313.15 K, and 323.15 K).

Temp	303.15K			313.15K			323.15K		
X_{MPK}	$\Delta G\times 10^{-19}$	$W\times 10^{-4}$	$R\times 10^{-4}$	$\Delta G\times 10^{-19}$	$W\times 10^{-4}$	$R\times 10^{-4}$	$\Delta G\times 10^{-19}$	$W\times 10^{-4}$	$R\times 10^{-4}$
0.000	-6.483	7.795	4.1958	-6.487	7.821	4.2126	-6.491	7.900	4.262
0.040	-6.483	8.342	4.4912	-6.489	8.350	4.4968	-6.493	8.462	4.567
0.086	-6.486	9.000	4.8494	-6.491	8.959	4.8244	-6.495	9.085	4.903
0.139	-6.490	9.708	5.2304	-6.493	9.688	5.2193	-6.496	9.816	5.299
0.200	-6.490	10.555	5.6881	-6.494	10.516	5.6659	-6.497	10.659	5.755
0.273	-6.492	11.531	6.2144	-6.494	11.496	6.1944	-6.499	11.649	6.291
0.361	-6.493	12.715	6.8538	-6.495	12.661	6.8225	-6.501	12.824	6.925

0.467	-6.495	14.139	7.6217	-6.498	14.103	7.6022	-6.503	14.238	7.686
0.601	-6.495	15.908	8.5754	-6.498	15.881	8.5615	-6.502	16.002	8.637
0.772	-6.497	18.177	9.8001	-6.501	18.159	9.7909	-6.503	18.277	9.864
1.000	-6.495	21.124	11.3863	-6.498	21.191	11.4286	-6.503	21.261	11.472





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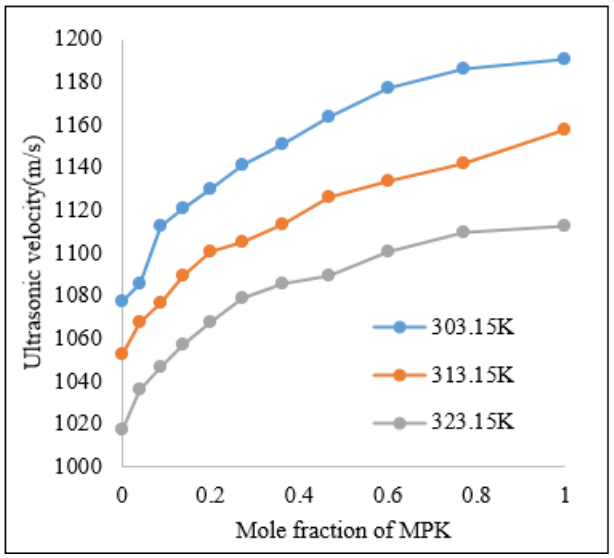

Figure 1: Variation of ultrasonic velocity V/S Mole fraction of MPK at various temperature

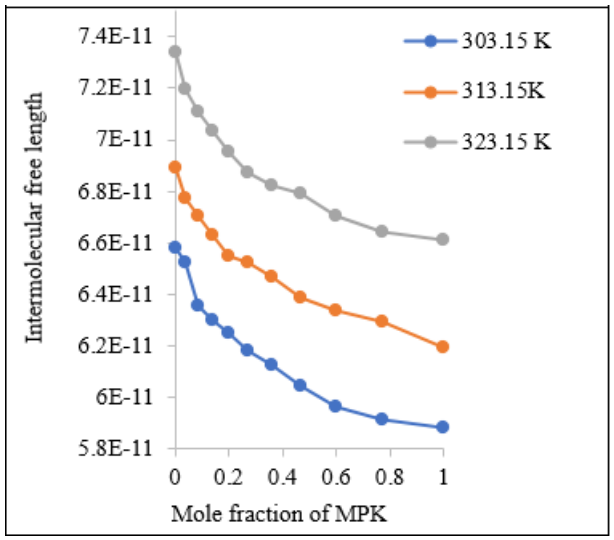

Figure 2: Variation of intermolecular free length V/S mole fraction of MPK at various temperature

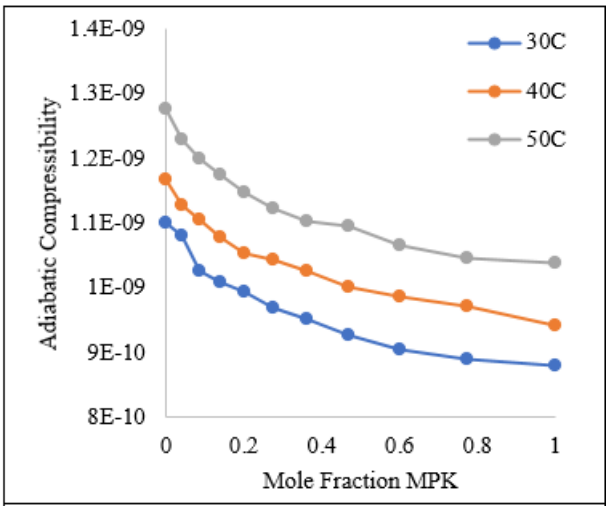

Figure 3: Variation of adiabatic compressibility V/S mole fractopn of MPK at various temperature

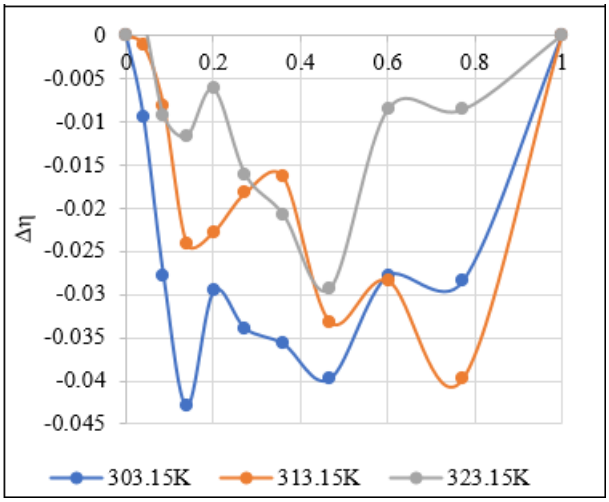

Figure 4: Variation of excess viscosity V/S mole fraction of MPK at various temperature

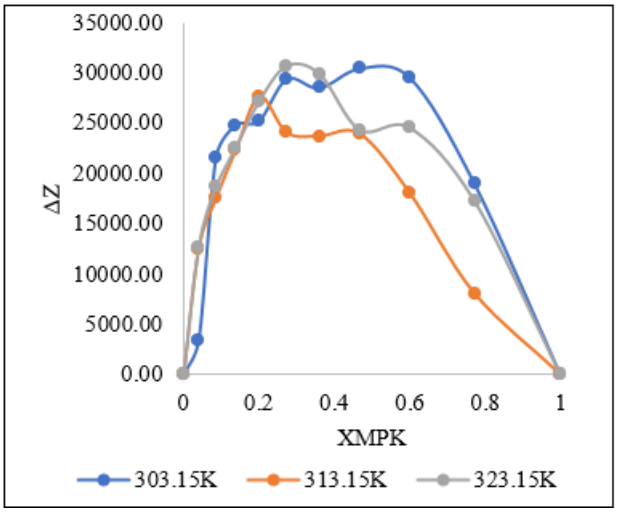

Figure 5: Variation of excess Acoustic impedence V/S mole fraction of MPK at various temperature

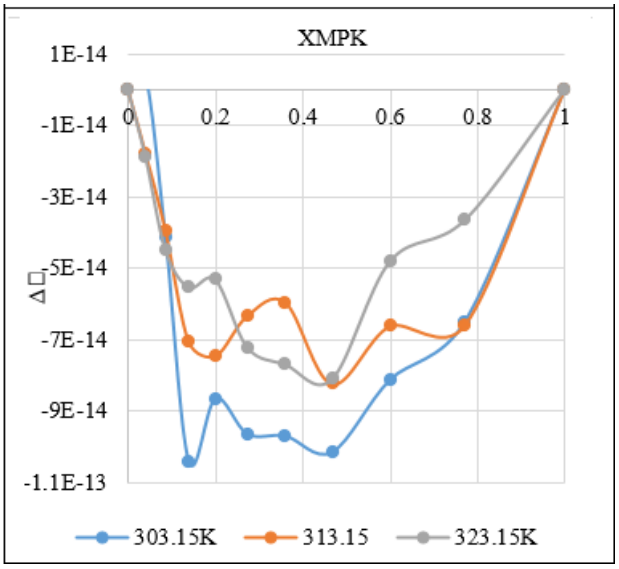

Figure 6: Variation of excess Relaxation Time V/S mole fraction of MPK at various temperature