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Study of intermolecular interaction of Allyl Chloride with 2-Pentanone and 2-Hexanone through excess molar volume and excess molar refraction

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ABSTRACT

In present paper, densities (ρ) and refractive indices (n_D) of allyl Chloride (AC) with 2-pentanone (2-PE) and 2-hexanone (2-HE) are measured on entire composition range and at different temperatures. We discuss the result of intermolecular interaction between allyl chloride and ketones (2-PE or 2-HE) in terms of excess molar volume and excess molar refraction which is determined from density and refractive index of binary mixtures. The system shows the opposite behaviour at AC rich region and ketone rich region. The excess parameters are subjected to Redlich- Kister polynomial equation.

Keywords: Molar refraction, excess molar volume, excess molar refraction

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INTRODUCTION

The emergence of combinatorial chemistry in drug discovery the measurement of physico-chemical parameters for a large number of compounds are required at a much earlier stage of the drug discovery process. Therefore it is apparent that knowledge of thermophysical properties such as density, refractive index, and related quantities are very useful for understanding and rationalizing the behavior of mixed liquids and their analytical applications. In this respect, the evaluation and the prediction of these properties of solvent mixtures as functions of temperature and composition are of theoretical and practical importance [1].

Allyl chloride is a highly versatile product due to its dual reactive sites at the double bond and the chlorine atom. It has found wide-spread use as a chemical intermediate in many industries and applications,[2] including the preparation of polymers, resins, and other plastic materials, increased oil production, the preparation and modification of catalysts, and the manufacture of pesticides, adhesives, flame retardants, chelating agents, detergents, dyestuffs, flavorings, metal brighteners, perfumes, pharmaceuticals, and urethanes. Ketones are produced on massive scales in industry as solvents, polymer precursors, and pharmaceuticals, especially for the solvating properties associated with its own character as an aprotic and protophilic medium. It is used in the industry of paints, varnishes, and printing inks.

Liang-sun Lee et al.[3] reported the excess molar volume positive for cyclohexane with 2-propanone, 2-butanone, 3-pentanone, 4-methyl-2-pentanone at temperature 298.15 K and 303.15 K. Comelli et al.[4] have published excess molar volume of diethyl carbonate + linear or cyclic ketones at 298.15 K. The nature of excess molar volume changes negative deviation to positive deviation as increases carbon chain in linear ketone. Roy et al.[5] reported the excess molar volumes of 2-butanone with 1,3-dioxolane 1,4-dioxane are negative indicate the specific interactions such as intermolecular hydrogen bonding between the mixing components and also the interstitial accommodation of the mixing components because of the difference in molar volume. Domanska et al.[6] reported excess molar volume of binary mixture of N-methyl-2- pyrrolidinone + ketone are negative for temperature 298.15 K.

The present paper devoted to study physical properties of ally Chloride in addition of Ketones. This is interested due to presence of negative inductive effect in allyl chloride and double bounded carbonyl group(C=O) in ketones. In other way functional group of ketone is polarized so that the carbon is electrophilic and the Chlorine is nucleophilic. The ketones are aprotic and protophilic medium, having carbonyl group (c=o) producing dipole. So it is interested to study intermolecular interaction between two different functional group molecules.

EXPERIMENTAL

Chemicals

The chemicals used in the present work are allyl chloride, 2-pentanone and 2-hexanone of AR grade and are used without further purification. The solutions were prepared at eleven

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different volume percentages of 2-PE or 2-HE 0% to 100% in steps of 10%, with accuracy ±0.0006ml

Measurement

Density determination by Pycnometer is a very precise method. Density of pure components and their binary mixtures were measured by using Pycnometer at temperatures 283.15 K, 293.15 K, 303.15 K and 313.15 K. Pycnometer volume is calibrated by double distilled water and acetone. The precision of density is 0.0001 gm/cm^3.

Refractive index of pure components and their binary mixture was measured at sodium D line by using thermostatic Abbe's refractometer at same temperature mentioned above. The precision of the refractive index is 0.001 units. Constant temperature maintained for density and refractive index measurement within the accuracy of ± 1^{0}C.

RESULTS AND DISCUSSION

The value of densities and refractive indices of pure liquids are tabulated in table 1 along with it's literature value. This shows the good agreement with literature value. The experimental value of densities and refractive indices of AC+2-PE and AC+2-HE are represented in table 2 and 3 respectively and graphical representations are shown in figure 1 and 2 respectively. The density and refractive index of two system decreases as concentration of Ketone (2-PE,2-HE) increases in binary mixture. The variations with respect to temperature in these parameters have also got usual trend, i.e. density and refractive index all parameters decrease with increase of temperature.

Table 1: Comparison of Physical parameters of 2-Pentanone, 2-Hexanone and Allyl Chloride

Liquids	Temp.	□ □ □ □ gm/cm^3		n_D	
		Lit	Expt.	lit	Expt.
2-Pentanone	283.15 k	-	0.8181	-	1.395
	293.15 K	0.809[a]	0.8086	1.3895[a]	1.389
	303.15 K	0.7966[b]	0.7994	-	1.385
	313.15 K	-	0.7894	-	1.380
2-Hexanone	283.15 k	-	0.8204	-	1.404
	293.15 K	0.8113[a]	0.8105	1.4007[a]	1.400
	303.15 K	-	0.8016	-	1.395
	313.15 K	-	0.7926	-	1.390
Allyl Chloride	283.15 k	-	0.9553	-	1.422
	293.15K	0.9376[a]	0.9442	1.4157[a]	1.416
	303.15 K	-	0.9316	-	1.411
	313.15 K	-	0.92014	-	1.407

[a] CRC Handbook 87th ed, [b]Patwari Murak Krishna

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Table2: Density and Refractive Index of Allyl Chloride with 2-Pentanone

Mole fraction of 2-PE	283.15 K		293.15 K		303.15 K		313.15 K	
	ρ (gm/cm^3)	n_D	ρ (gm/cm^3)	n_D	ρ (gm/cm^3)	n_D	ρ (gm/cm^3)	n_D
0	0.9553	1.422	0.9442	1.416	0.9356	1.411	0.9223	1.407
0.0780	0.9384	1.419	0.9279	1.413	0.9182	1.408	0.9050	1.403
0.1598	0.9269	1.416	0.9163	1.410	0.9054	1.405	0.8924	1.400
0.2459	0.9177	1.414	0.9071	1.408	0.8961	1.403	0.8836	1.398
0.3365	0.9089	1.412	0.8977	1.406	0.8864	1.401	0.8746	1.396
0.4321	0.9018	1.410	0.8902	1.404	0.8790	1.399	0.8675	1.394
0.5330	0.8925	1.408	0.8812	1.402	0.8699	1.397	0.8586	1.392
0.6397	0.8776	1.406	0.8656	1.400	0.8547	1.395	0.8441	1.390
0.7527	0.8591	1.404	0.8477	1.398	0.8370	1.393	0.8269	1.388
0.8726	0.8383	1.401	0.8280	1.395	0.8176	1.39	0.8078	1.385
1	0.8181	1.395	0.8086	1.389	0.7994	1.385	0.7894	1.380

ρ-density, n_D-Refractive index , uncertainty in density measurement is 0.0002%

Table3: Density and Refractive Index of Allyl Chloride with 2-Hexanone

Mole fraction of 2-HE	283.15 K		293.15 K		303.15 K		313.15 K	
	ρ (gm/cm^3)	n_D	ρ (gm/cm^3)	n_D	ρ (gm/cm^3)	n_D	ρ (gm/cm^3)	n_D
0	0.95533	1.422	0.94415	1.416	0.93160	1.411	0.92014	1.407
0.0679	0.93922	1.420	0.92589	1.413	0.91382	1.409	0.90192	1.404
0.1409	0.91982	1.418	0.90856	1.412	0.89595	1.408	0.88513	1.402
0.2194	0.90835	1.417	0.89673	1.411	0.88568	1.407	0.87542	1.401
0.3042	0.89974	1.416	0.88894	1.410	0.87798	1.407	0.86736	1.400
0.3961	0.89129	1.415	0.88022	1.409	0.86926	1.405	0.85893	1.399
0.4959	0.88187	1.413	0.87029	1.408	0.85965	1.404	0.84967	1.397
0.6048	0.86855	1.411	0.85827	1.406	0.84820	1.403	0.83818	1.396
0.7240	0.85584	1.409	0.84598	1.404	0.83630	1.401	0.82675	1.394
0.8551	0.84285	1.406	0.83342	1.402	0.82328	1.400	0.81368	1.392
1	0.82041	1.404	0.81046	1.400	0.80160	1.395	0.79263	1.390

ρ-density, n_D-Refractive index

The excess molar volume, excess molar refraction are very important to better understanding the intermolecular interaction between two components involved in complex.

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Figure 1: Excess molar volume of Allyl Chloride with 2-Pentanone

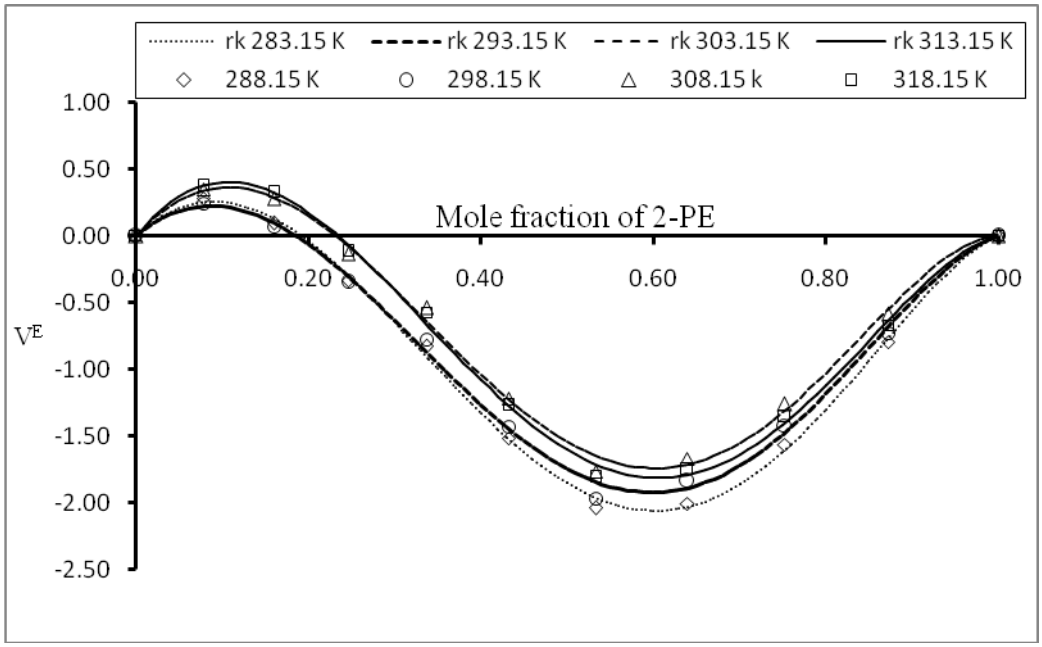
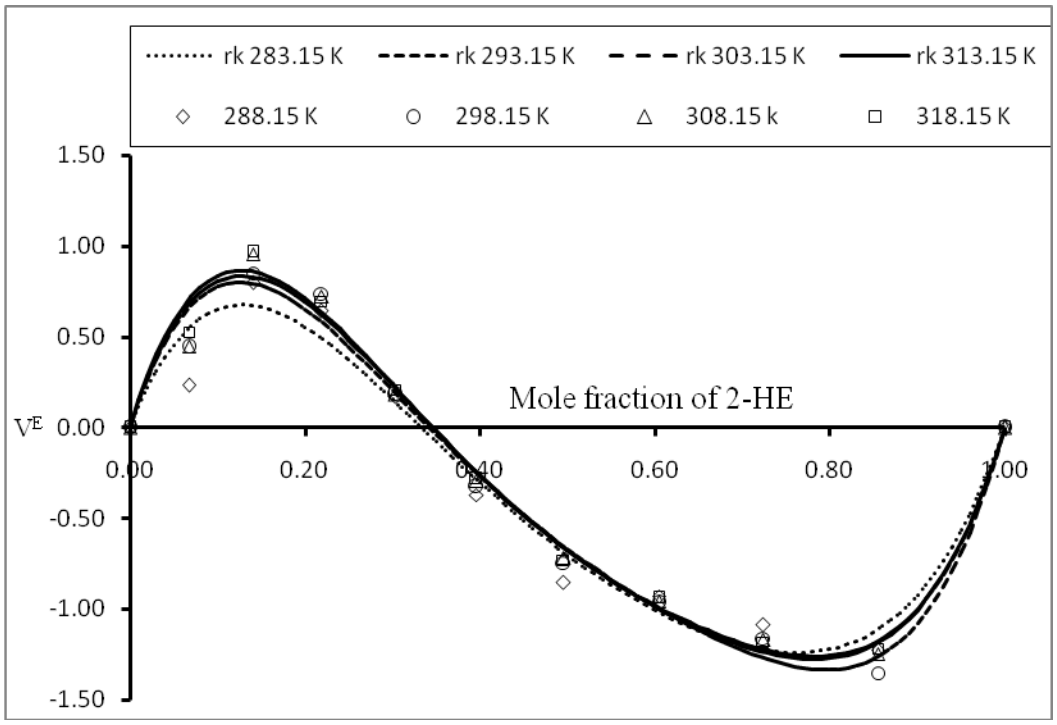


Figure 2: Excess molar volume of Allyl Chloride with 2-Hexanone



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The excess molar volume of mixtures are determined by

$$V^E = \left[\frac{X_1M_1+X_2M_2}{\rho}\right] - \left[\frac{X_1M_1}{\rho_1} + \frac{X_2M_2}{\rho_2}\right] \quad (1)$$

where, ρ is the density of the mixture, X_1, X_2, M_1, M_2 and ρ_1 and ρ_2 are the mole fraction, molar mass and the density of pure Allyl Chloride and Ketones(2-PE,2-HE) in composition respectively.

The evaluated values of excess molar volume are plotted in figure 1 and 2 for system AC+2-PE and 2-HE respectively. The dependence of V^E [7,8,9,] on both composition and temperature for the present mixtures may be explained as a balance between positive contributions and negative contributions. The positive contribution arises from dispersion forces or weak dipole-dipole interaction between unlike molecules, due to hydrogen bond rupture. The negative contribution from specific interactions which include charge transfer, formation of hydrogen bonds, and the structural contributions due geometrical fitting of one component into another due to difference in molar volumes.

The positive value V^E (upto 0.2 Mole fraction of 2-PE in AC+2-PE system and upto approximately 0.35 Mole fraction of 2-HE in AC+2-HE) as result of dispersion interaction between two mixing component arises due to breaking of cohesive force in like molecule and weak dipole-dipole interaction of AC with Ketone. The negative values V^E (above 0.2 Mole fraction of 2-PE in AC+2-PE system and above approximately 0.35 Mole fraction of 2-HE in AC+2-HE) are contributed from adhesive force between two mixing component are large and dipole-dipole interaction goes on increasing due high polarity Ketones concentration increases.

The molar refraction (R_m) are related to both refractive index and molecular properties of compound. The R_m value of compound can be often being predicated structural feature of molecule [10]. Each constituent atom or groups contribution portion to final R_m value in connection with additive constituent properties. We have investigated the molar refraction R_m defined by Lorenz-Lorenz [11] equation

$$R_m = \frac{n_D^2-1}{n_D^2+1}V_m \quad (2)$$

The molar refraction for present both systems are plotted in figure 3 and 4. This plot shows that, it is independent on temperature.

Excess molar refraction is also important parameter for study of intermolecular interaction. It is determined by using equation

$$R_m^E = R_m - (X_1R^1{}_m + X_2R^2{}_m) \quad (3)$$

where $R^1{}_m$ and $R^2{}_m$ are molar refraction of the pure AC and Ketone respectively.

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R_m gives the strength of interaction in mixture and it is function of wavelength of light used, temperature and concentration [11, 12]. Magnitude and sign of excess molar refraction give strength of molecular interaction. The R_m^E graphically represented for system AC+2-PE and AC+2-HE in figure5 and 6 respectively, which shows that R_m^E values are positive (below 0.2 mole fraction of 2-PE and 0.4 mole fraction of 2-HE) indicating presence of weak intermolecular interaction. The R_m^E values are negative (above 0.2 mole fraction of 2-PE and 0.4 mole fraction of 2-HE except above 0.92+HE) indicating the presence of strong intermolecular interaction.

Figure 3: Molar Refraction of Allyl Chloride with 2-Pentanone

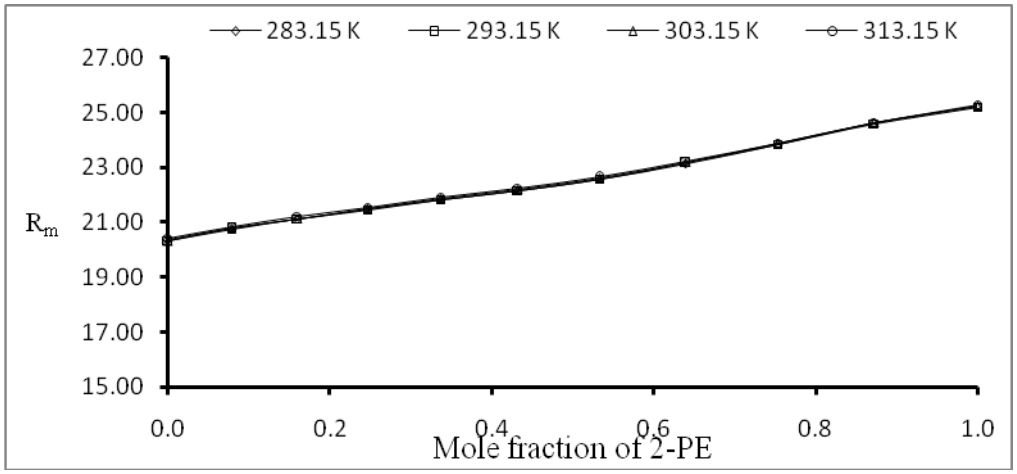


Figure 4: Molar Refraction of Allyl Chloride with 2-Hexanone

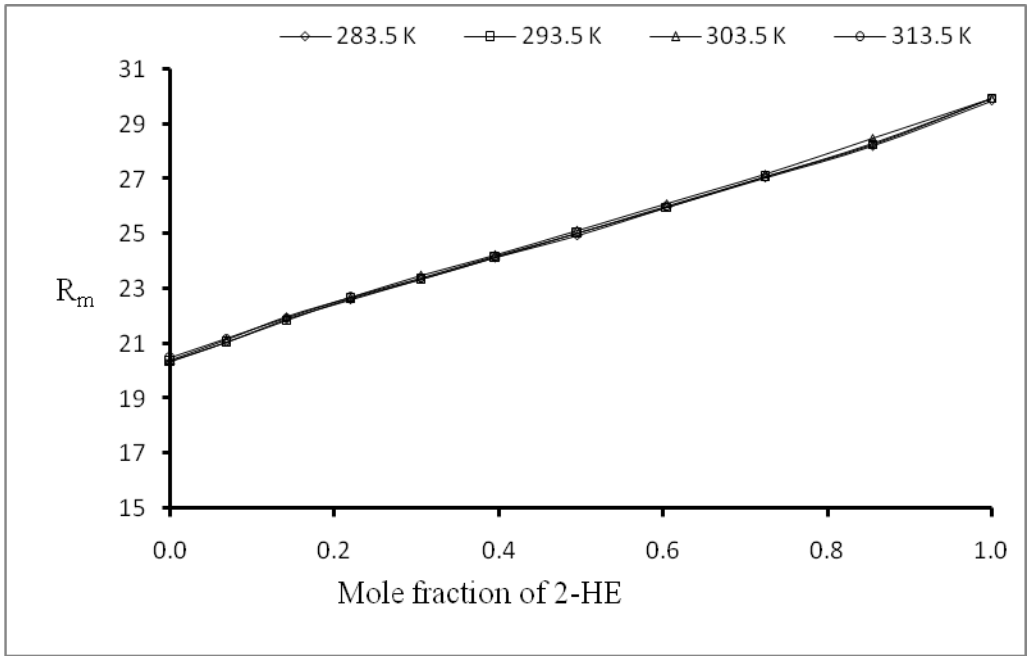


Figure 5: Excess molar Refraction of Allyl Chloride with 2-Pentanone

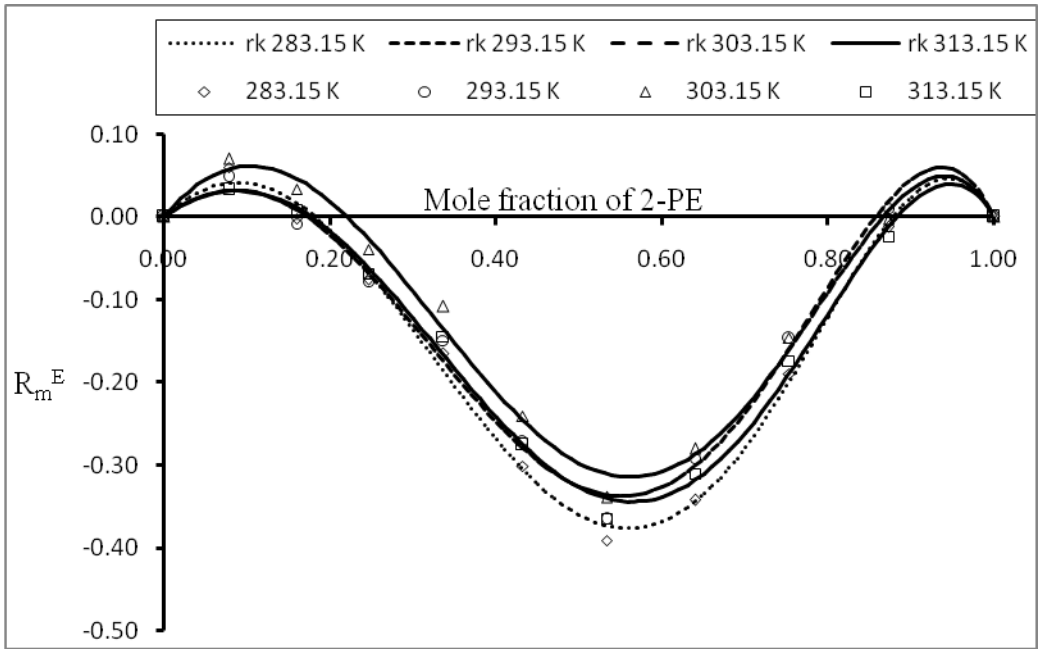
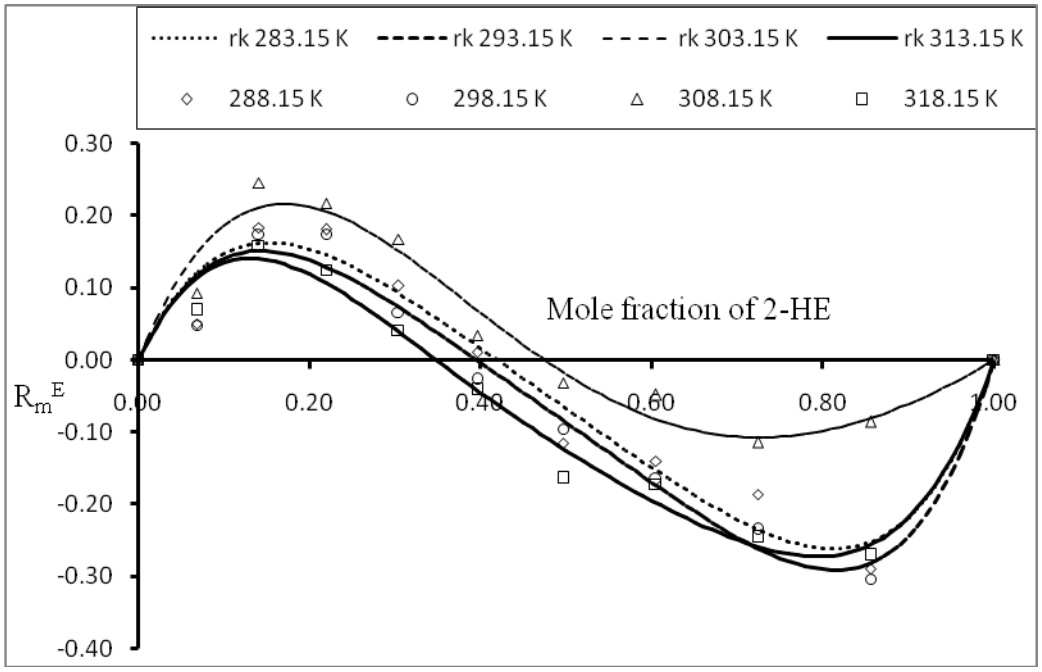


Figure 6: Excess molar Refraction of Allyl Chloride with 2-Hexanone



The excess molar volume and excess molar refraction were fitted to Redlich-Kister equation [13] given by

$$Y^E = X(1-X)\sum_{j=0}^{3} a_j(2X-1)^j \qquad (4)$$

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And the standard deviation is obtained by the expression

$$\sigma = \sqrt{\frac{[\sum V^E_{cal} - V^E_{expt}]^2}{(n-1)}} \quad (5)$$

where Y^E refers to be an V^E or $R_m{}^E$ for binary mixture and (1-X)is the mole fraction of the Allyl Chloride, X is mole fraction of Ketones, a_j represent the adjustable coefficients and n is the experimental data points. The a_j coefficient and standard deviation for excess molar volume and excess molar refraction are reported in table 4.

Table 4: a_j coefficients and standard error (σ)

Excess parameters	Temperatures	a_0	a_1	a_2	a_3	σ
	AC+2-PE					
V^E	283.15 K	-7.4244	-7.7300	8.9314	3.2361	0.0513
	293.15 K	-6.9908	-6.9815	8.5610	3.1763	0.0719
	303.15 K	-6.1862	-7.4229	9.5386	3.5944	0.0680
	313.15 K	-6.4210	-7.7780	9.5827	2.8793	0.0583
$R_m{}^E$	283.15 K	-1.4404	-1.0867	2.8187	1.5221	0.0156
	293.15 K	-1.3045	-0.8713	2.7027	1.5213	0.0194
	303.15 K	-1.1910	-1.0456	2.6828	1.3288	0.0186
	313.15 K	-1.3082	-1.0595	2.4697	1.5064	0.0154
	AC+2-HE					
V^E	283.15 K	-2.8135	-7.0962	2.0309	-6.0021	0.1759
	293.15 K	-2.6773	-7.0841	1.5316	-9.0744	0.1254
	303.15 K	-2.6998	-7.2317	2.4650	-8.3492	0.1185
	313.15 K	-2.7112	-7.0841	2.8074	-8.8345	0.0931
$R_m{}^E$	283.15 K	-0.2705	-1.6675	-0.1825	-1.3634	0.0441
	293.15 K	-0.3483	-1.6685	-0.3494	-1.5649	0.0363
	303.15 K	-0.0793	-1.4977	1.2147	-0.3377	0.0319
	313.15 K	-0.5036	-1.5022	0.0672	-1.4751	0.0280

CONCLUSION

From experimental result and discussion, we are come to the conclusion as follow

- The positive excess molar volume and excess molar refraction in Ally chloride rich region is reflection of weak intermolecular interaction
- The negative excess molar volume and excess molar refraction (except 0.9 mole fraction of 2-PE) in Ketone rich region indication of strong intermolecular interaction.
- The change of positive to negative trend of excess molar volume and excess molar refraction shifted towards higher concentration of Ketones due to increases in carbon chain of Ketone only.
- Thus intermolecular interaction of Allyl Chloride with 2-Hexanone are weaker than 2-Pentanone.

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