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Study of Intermolecular Interaction of Allyl Bromide with 2-Pentanone and 2-Hexanone through the Thermodynamics properties.

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ABSTRACT

The present paper, the Density and Refractive index of binary mixture of Allyl Bromide (ALB) with 2-Pentanone (2-PE) and Allyl Bromide with 2-Hexanone are measured at various concentration and at temperature 293.15K, 303.15K and 313.15 K. The measured Density and Refractive index are further used to evaluation of excess molar volume and excess molar refraction. The excess values are used to study the intermolecular interaction between Allyl Bromide (ALB) with 2-Pentanone (2-PE) and 2-Hexanone (2-HE). The excess parameters are fitted to Redlich-Kister polynomial equation. The excess values of binary mixture shows opposite tendency in ALB rich region and 2-Pentanone (or 2Hexanone) rich region. The study reveals that behavior of weak adhesive force between ALB with 2-Pentanone and 2-HExanone in ALB rich region and strong adhesive force in Ketone (2-PE, 2-HE) rich region and geometrical fitting of components one each other.

Keyword: Density, Refractive Index, excess molar volume, excess molar refraction,

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INTRODUCTION

Thermodynamics properties is one of important properties to extract insight information of binary mixture. Many researchers study the thermodynamics parameter such as density, refractive index and their excess values provide us to insight into nature, types and strength of molecular interaction. It also provides deviation from ideality. These data further used in industries, thermodynamics and engineering. Thermodynamics properties key parameter for understanding physico chemical behavior of binary mixture. Allyl bromide is electrophilic alkylating agent used in synthesis of polymer, pharmaceutical perfumes etc. The binary mixture may be form complex due to polar interaction, dipole –dipole interaction, hydrogen bonding. 2-Pentanone and 2-Hexanone have carbonyl group that interact with electron deficiency in allyl bromide functional group bromine. These concept leads to distinct excess properties which is differ from ideal mixture.

Density and Refractive index are fundamental properties and very useful to access the change in internal structure of mixture. Density measures the change in complex form of two molecules fitted or not fitted. The refractive index measure strength of interaction of light through medium.

Prakash et.al [1] reported densities, viscosities and sound velocities of o-Chlorophenol with Acetone and Ethyl Methyl ketone systems at 25°C Awwad et.al [2] reported the density, refractive index, permittivity and related properties for *N*-Formylmorpholine with Ethyl Acetate and + Butanone systems at 298.15 K. Lomte et.al [3] studied the densities and viscosities of binary liquid mixtures of 2-Butanone with branched alcohols at different temperature. Ouyang et.al [4] studied excess molar volumes and surface tensions of Xylene with Acetone or 2-Butanone at 298.15 K. He found excess molar volume of mixtures is negative. Tojo et.al [5] studied dynamic viscosities of the binary systems of Cyclohexane and Cyclopentane with Acetone, Butanone, or 2-Pentanone at temperature 293.15, 298.15, and 303.15 K. Liang-Sun Lee et.al [6] reported the positive excess molar volume of Cyclohexane+ketone mixtures. Clara et.al [7,8] studied density, viscosity, refractive index and related excess properties of 2-Butanone with Chloroform and 1-Butanol, negative excess molar volume for all temperature and composition shows the interaction between different molecule are stronger than interaction between molecule of pure liquids. Baraldi et.al [9] studied density, refractive index and related properties of 2-Butanone with n-Hexane at various temperature. Ming Jer Lee et.al [10] studied density and viscosity of 2-Butanone with Dibutyl ether and 2-Picoline binary mixtures.

In early, our research group [11-14] reported the dielectric properties and thermodynamics properties of Allyl chloride with ketone such as 2-Butannaone, 2-Petnatanone 2-Hexanone. This paper represent the extend of our work for ALB with 2-PE and 2-HE at temperature 293.15K, 303.15K and 313.15K.

EXPERIMENTAL

The chemical used in these present work are Allyl Bromide, 2-Pentanone and 2-Hexanone of AR grade and used without further purification. The 5 mL solutions were prepared at eleven different volume percentages by adding 2-PE(or 2-HE) in Allyl Bromide starting from 0-100 % in steps of 10 %, by micropipette with an accuracy of ± 0.0006 ml.

Density of pure components and their binary mixtures were measured by using Pycnometer at temperatures 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/cm3.

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 ± 1^0C.

Theory

Molar volume is derived from density and used for excess molar volume. Excess molar volume of binary mixture is direct evidence of intermolecular interaction involved in mixture. The positive excess molar volume indicates weak intermolecular interaction while negative indicates that strong

intermolecular interaction [15,16]. Excess molar volume is defined as

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

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 Bromide and 2-PE (or 2-HE) in composition respectively.

Molar refraction is related to both refractive index and molecular properties of binary mixture. Molar refraction value of compound can be often predicated from structural feature of molecule. Each constituent atom or group of atoms contributes to final molar refraction value in connection with additive constitutive properties. Molar refraction R_m defined by Lorenz-Lorenz equation

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

R_m gives the strength of interaction in mixture and it is function of wavelength of light used, temperature and concentration [17]. Magnitude and sign of excess molar refraction give strength of molecular interaction [18]. Excess molar refraction determined by

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

Where R_m^1 and R_m^2 are molar refraction of one and second component respectively

The excess molar volume and excess molar refraction fitted to the Redlich – Kister [19-20] equation.

$$Y^E = x\ .(1-x).\sum_{j=0}^{n} a_j.(2x\ -1\ )^j \quad (4)$$

and standard deviation(σ) is determined by

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

RESULT AND DISCUSSION

The values of density and refractive index of ALB with 2-PE and ALB with 2-HE are tabulated in Table 1 and 2 respectively. From table 1 and 2, it is observed that density of binary mixture decreases as concentration of 2-PE(or 2-HE) increases. The density of ALB+2-HE is greater than ALB+2-PE at every same concentration. It is also observed that density of mixture decreases as temperature of mixture increases for both systems.

The interpretation of V^E can explain either physical, chemical and structural effect [21]. The experimental observation on volumetric changes are very useful for understanding that the kind of effects are responsible for the degree of molecular packing and macroscopic behaviour of mixtures. For present systems Excess molar volume for ALB+2-PE and ALB-2HE are plotted in figure 1 and 2 respectively. The both system reveals somewhat similar nature on volumetric changes i.e. The positive value of excess molar volume in ALB rich region suggests that weak adhesive force (hetero dipole –dipole force) and rupture of cohesive force. It will maximum at about 0.25 mole fraction of 2-PE (2-HE), Above this concentration this phenomenon of interaction goes on decreasing and at 0.4 mole fraction of 2-PE (2-HE). It will reveal the exact opposite in 2-PE (2-HE) rich region. The negative excess molar volume suggests that strong intermolecular interaction. The structural effect that arises from geometrical fitting of one component into other are due to different molar volumes and free volumes of pure components and lead to negative contribution to V^E. It shows minimum at 0.7 mole fraction of 2-PE (2-HE). The effect of temperature on excess molar volume is observed small but not significant.

Molar refraction gives the strength of interaction in mixtures and it is a function of wavelength of light used, temperature and concentration [17]. The result of excess molar refraction plotted in fig. 3 and 4 respectively. These are supported to result obtained from excess molar volume. The magnitude of R_m^E decreases with increase in temperature indicates molecular interaction decreases with rise in temperature of mixtures [23]. The excess molar volume and excess molar refraction are fitted to Redlich –Kister equation. The RK coefficient a_j' s are determined by RK equation and tabulated in table 3 with standard deviation.

Table 1: Density (gm/cm³) and Refractive index of Allyl Bromide +2-Pentanone binary System.

Mole fraction of 2-PE	293.15 K		303.15 K		313.15 K	
	ρ	n_D	ρ	n_D	ρ	n_D
0	1.3980	1.467	1.3813	1.460	1.3645	1.455
0.0828	1.3357	1.456	1.3179	1.450	1.3037	1.444
0.1688	1.2610	1.446	1.2450	1.440	1.2308	1.434
0.2582	1.1926	1.438	1.1783	1.432	1.1643	1.426
0.3513	1.1525	1.432	1.1394	1.426	1.1250	1.420
0.4482	1.1166	1.427	1.1017	1.421	1.0900	1.416
0.5492	1.0730	1.422	1.0606	1.416	1.0480	1.411
0.6546	1.0321	1.417	1.0200	1.412	1.0073	1.406
0.7647	0.9705	1.410	0.9587	1.405	0.9478	1.399
0.8797	0.8908	1.401	0.8810	1.396	0.8702	1.390
1	0.8086	1.389	0.7994	1.386	0.7895	1.380

Table 2: Density (gm/cm³) and Refractive index of Allyl Bromide + 2-Hexanone binary system.

Mole fraction of 2-HE	293.15 K		303.15 K		313.15 K	
	ρ	n_D	ρ	n_D	ρ	n_D
0	1.3980	1.467	1.3813	1.460	1.3645	1.455
0.0722	1.3379	1.458	1.3216	1.450	1.3062	1.445
0.1490	1.2615	1.450	1.2462	1.442	1.2318	1.437
0.2308	1.1912	1.443	1.1769	1.436	1.1628	1.431
0.3183	1.1562	1.438	1.1417	1.431	1.1286	1.426
0.4119	1.1190	1.433	1.1057	1.427	1.0934	1.421
0.5123	1.0786	1.428	1.0661	1.423	1.0538	1.418
0.6203	1.0345	1.423	1.0226	1.418	1.0110	1.413
0.7369	0.9755	1.416	0.9643	1.411	0.9536	1.406
0.8631	0.8947	1.408	0.8846	1.403	0.8747	1.398
1	0.8105	1.399	0.8016	1.395	0.7926	1.390

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Table 3: a_j coefficient and standard deviation (σ) of excess parameters.

		a_0	a_1	a_2	a_3	σ
293.15K						
ALB+2-PE	V^E	-7.4787	-43.5937	-1.6683	37.1338	0.2866
	R_m^E	-1.5057	-8.3195	-0.5688	7.2775	0.0690
ALB+2-HE	V^E	-12.0993	-46.8694	7.1605	38.3979	0.4214
	R_m^E	-2.6330	-9.8363	1.3357	9.1591	0.1068
303.15K						
ALB+2-PE	V^E	-7.4043	-43.6680	-1.5367	35.3587	0.2553
	R_m^E	-1.5870	-7.6930	-0.3725	5.8003	0.0649
ALB+2-HE	V^E	-12.0475	-47.7336	7.6177	39.2380	0.4162
	R_m^E	-2.6008	-9.6591	0.4807	9.1258	0.1132
313.15K						
ALB+2-PE	V^E	-7.6841	-44.5513	-2.1633	37.3156	0.2856
	R_m^E	-1.7146	-7.6901	-0.7447	6.4787	0.0737
ALB+2-HE	V^E	-12.2921	-48.2596	7.3858	40.0019	0.4429
	R_m^E	-2.6898	-9.4684	0.5346	8.8858	0.1282

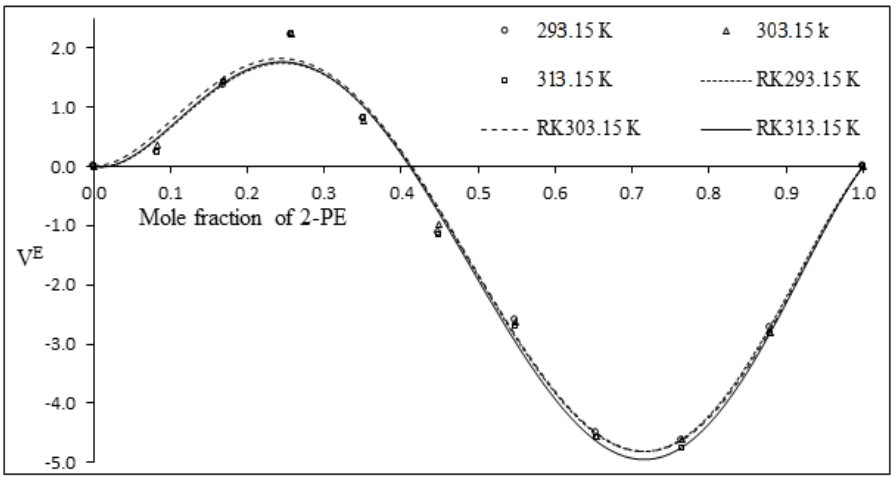

Figure 1: Excess molar volume (V^E)of Allyl Bromide +2-Pentanone binary System

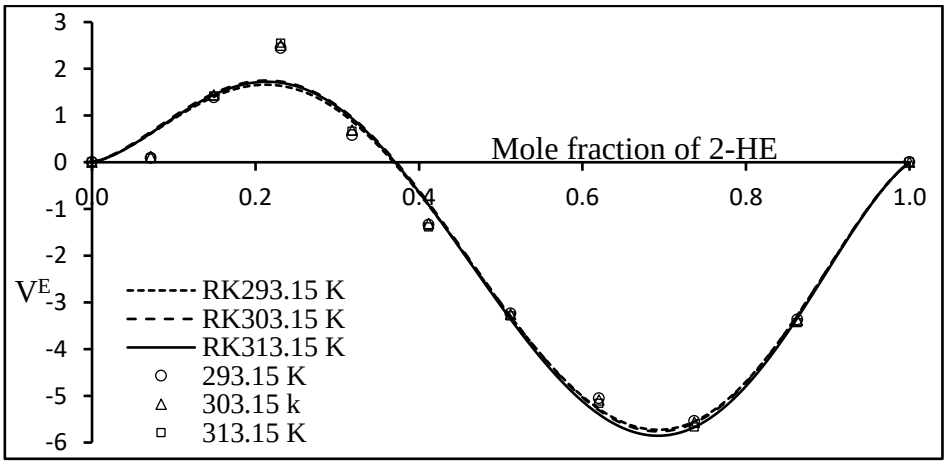

Figure 2: Excess molar volume (V^E) of Allyl Bromide +2-Hexanone binary system

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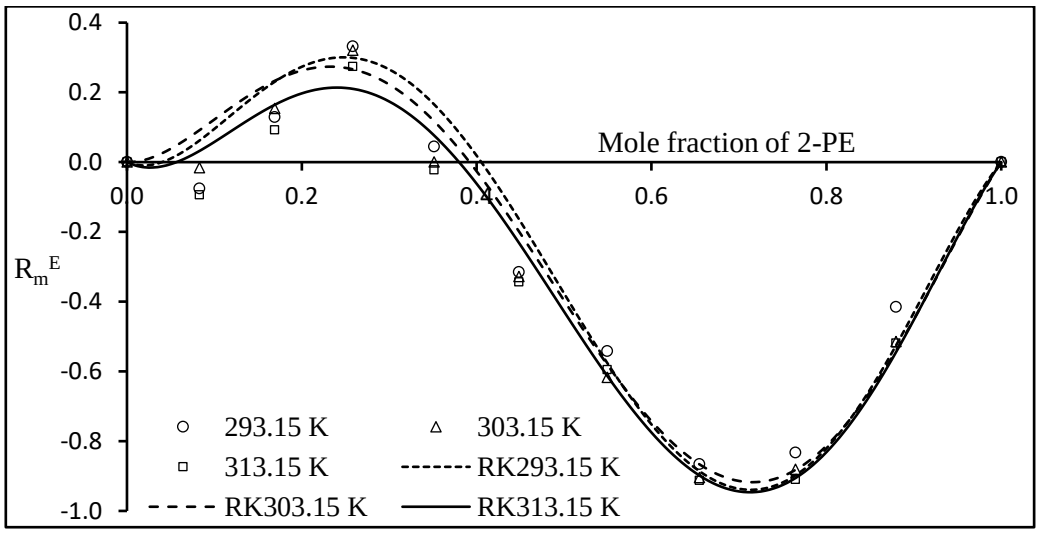

Figure 3: Excess molar refraction (R_m^E) of Allyl Bromide +2-Pentanone binary system

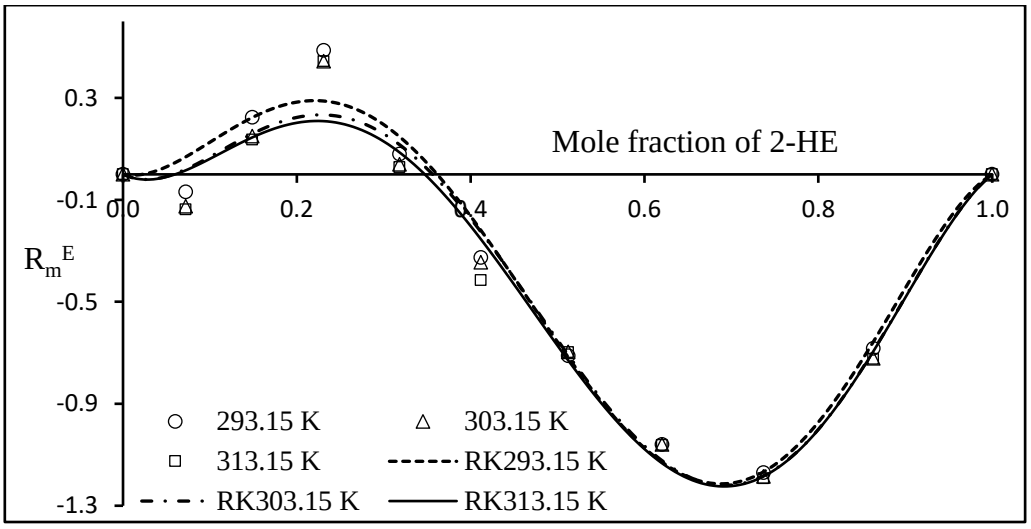

Figure 4: Excess molar refraction R_m^E of Allyl Bromide +2-Hexanone binary System

CONCLUSION

The non-linear behavior of density and refractive index at temperature 293.15K 303.15K and 313.15K show that intermolecular interaction take place between ALB and 2-PE(or 2-HE). The effect of temperature on density and refractive index observed as usual trends. i.e. it decreases with increases in temperature.

The excess molar volume and excess molar refraction of both system are supported to each other. The opposite trends of excess molar volume as well as excess molar refraction in ALB rich region show that weak intermolecular interaction between ALB and 2-PE(or 2-HE) while in 2-PE rich region shows that strong intermolecular interaction .

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