



Assessing How Thermodynamic Properties Varies for Ethyl Acetate and N-Pentanol System at Dualistic Temperatures

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ABSTRACT: For any liquid mixtures, the study of thermodynamic properties is very crucial as they provide a valuable source of information. The data of these binary mixtures for the chemical industries have to be very reliable as they provide a continuous feed that helps in the design process for chemical separation heat transfer, mass transfer, fluid flow, and many others. In this process, the present study is focused on thermodynamic and excess thermodynamic properties for a binary mixture of n-Pentanol with ethyl acetate. After calculating all the thermodynamic properties, excess parameters were also calculated to test the system's reliability and the values thus obtained are fitted into the Redlich – Kister equation. Moreover to compare Ultrasonic velocities theoretical relations of Nomoto and Van Dael Vangeel were used. These properties can be commendably utilized as a qualitative study to predict the extent of molecular interactions between the components.

Keywords: Adiabatic Compressibility, Intermolecular forces, Nomoto, Ultrasonic Velocity, Viscosity, Van Dael and Vangeel.

I. INTRODUCTION

From the past few years, examining and assessing the thermodynamic properties of liquid mixtures has been ever increasing. The thermodynamic properties of liquids in any binary mixture depict substantial weight on the physical and chemical properties [1-5]. These properties provide better information necessary for understanding the non-ideal behavior of complex systems, which are caused by molecular interactions, dipole-dipole interactions etc., of different molecules. In the practical world, these properties are very much looked-for the diverse areas like bio-chemical, Food industry, metallurgy, molecular dynamics studies and what not. It is the year of 1931 which paved a new path that. Till 1931 no one knows how can solutions deviates from its ideal behavior, but in the same year Scatchard proposed an equation which solved afore mentioned problem with the excess thermo dynamic parameters which are shown below, where excess thermodynamic parameters denoted by super script E.

$$Y^E = Y_{\text{real}}^M \cdot Y_{\text{ideal}}^M$$

Initially Vander Waals and Van Laar [6] proposed the theories for binary liquid mixtures which successfully explained many properties to the certain extent. To further improve Van Laar's theory, Hildebrand and Scott [7] and Scatchard [8-11] used Hildebrand's [12] developed a concept of regular solutions and there by correlated with excess volume.

Redlich and Kister [13] derived an experimental equation to predict Y^E values for binary liquid mixtures.

$$Y^E = X_1 X_2 [A_0 + A_1 (X_1 - X_2) + A_2 (X_1 - X_2)^2]$$

Where A_0 , A_1 and A_2 are constants X_1 , X_2 are the mole fractions of the two different components.

Rao [14] found that the thermal coefficient of ultrasonic velocity in organic liquids is about three times the thermal coefficient of density.

$$R = U^{1/3} V,$$

Where R is known as molar sound velocity constant.

Jacobson [15] derived an empirical relation between three thermodynamic parameters (ultrasonic velocity, density, and intermolecular free length). Survey on literature reveals the great volume of work has been carried out in binary and ternary systems for weak and strongly interacting systems but only a few studies are reported with Ethyl acetate as the main component, and no thermodynamic studies were conducted at 303.15K and 313.15K. To have a piece of precise knowledge about the molecular interactions; ultrasonic velocities, densities, viscosities and theoretical relations of Nomoto; Van Dael and Vangeel of Ethyl acetate +n-pentanol at two temperatures have been studied.

II. METHODOLOGY

The ultrasonic velocity measurements are made with the help of a single crystal ultrasonic pulse echo-interferometer. The densities of the liquid mixture (Ethyl Acetate + n-Pentanol) have been determined by using a single pan electrical balance for the determination of mass of a given volume of the liquid. The coefficient of viscosity has been determined as a function of composition and temperature, using the Oswald's viscometer. The temperature of the mixture is maintained at the required constant value by using constant temperature bath, controlled by thermostat with an accuracy of ± 0.01 K. All the excess parameters are

fitted into the Redlich – Kister equation. The values of parameters obtained by Cramer's rule are included with the standard deviation(σ). The excess volumes of mixing have been evaluated both as a formation of composition and temperature to examine the possibility of structural adjustment. To have a clear knowledge the Present Study has been divided into 3 parts. An attempt has been made to compare the merits of the relations for the binary liquid mixtures investigated at different temperatures. The deviation in the variation of U_{exp}^2 / U_{mix}^2 from unity has also been evaluated for explaining the non-ideality in the mixture.

III. RESULTS AND DISCUSSION

All the measured values like, ultrasonic velocity (U) density (ρ), viscosity(η), molar volume (V_m), adiabatic compressibility (β_{ad}), intermolecular free length (L_f), Rao's Constant(R) and Wada's Constant (W) along with excess molar volume (V_m^E), excess intermolecular free length (L_f^E), deviations in adiabatic compressibility ($\Delta\beta_{ad}$)

and deviations in viscosity ($\Delta\eta$) of the binary mixture and had been measured for the chosen two temperatures. All the calculated parameters were presented from tables 1 to 3. The results are interpreted in terms of intermolecular interactions between the components of the mixtures.

Ultrasonic velocity (U) in this system is plotted with respect to mole fraction of ethyl acetate in Fig. 1(A) for different temperatures which represents that the velocity decreases non-linearly and the decrease in ultrasonic velocity in any solution indicates the maximum association among the molecules of the solution. Density variation, dependence of viscosity (η), and deviation in viscosity($\Delta\eta$) had shown in Fig. 1(B), 2(A) and 6(C) respectively. The viscosity curves show positive deviations maximum at about 0.52 mole fraction and is favoring the dipole-dipole interactions. The variation of molar volume (V) and excess molar volume (V^E) is shown in Figs. 2(D) and 5(A) respectively.

Table 1: Variation of U, ρ , η , V_m at temperatures 303.15K AND 313.15K.

| Mole Fraction X | Ultra sonic Velocity(U)m/s | | $\rho \times 10^{-3} \text{kg/m}^3$ | | ηCp | | $V_m \text{cm}^3 \text{mol}^{-1}$ | |
|-----------------|----------------------------|---------|-------------------------------------|---------|------------------|---------|-----------------------------------|----------|
| | 303.15K | 313.15K | 303.15K | 313.15K | 303.15K | 313.15K | 303.15K | 313.15K |
| 0.0000 | 1264.50 | 1228.50 | 0.8087 | 0.8009 | 3.7310 | 2.8906 | 109.0021 | 110.0637 |
| 0.1088 | 1251.94 | 1213.44 | 0.8276 | 0.8230 | 3.4031 | 2.6413 | 106.5104 | 107.1042 |
| 0.2156 | 1237.39 | 1197.99 | 0.8442 | 0.8416 | 3.0749 | 2.3993 | 104.4095 | 104.7247 |
| 0.3202 | 1222.85 | 1182.41 | 0.8595 | 0.8569 | 2.7527 | 2.1578 | 102.5389 | 102.8546 |
| 0.4229 | 1208.39 | 1166.26 | 0.8730 | 0.8708 | 2.4310 | 1.9164 | 99.7062 | 99.9708 |
| 0.5237 | 1193.37 | 1150.55 | 0.8839 | 0.8815 | 2.1051 | 1.6701 | 99.0530 | 99.2659 |
| 0.6225 | 1179.44 | 1134.85 | 0.8897 | 0.8878 | 1.7655 | 1.4111 | 98.7379 | 98.9483 |
| 0.7195 | 1163.94 | 1120.13 | 0.8925 | 0.8906 | 1.4235 | 1.1486 | 98.6303 | 98.9377 |
| 0.8147 | 1148.36 | 1105.89 | 0.8934 | 0.8906 | 1.0843 | 0.8875 | 98.7698 | 99.4235 |
| 0.9082 | 1132.90 | 1090.62 | 0.8921 | 0.8862 | 0.7456 | 0.6258 | 99.1560 | 100.6052 |
| 1.0000 | 1115.90 | 1076.00 | 0.8886 | 0.8758 | 0.4038 | 0.3652 | | |

Table 2: Variation of β_{ad} , L_f , R, W at Temperatures 303.15K and 313.15K.

| Mole Fraction X | $\beta_{ad} 10^{12} \text{m}^2 \text{N}^{-2}$ | | $L_f 10^{-10} \text{m}$ | | R | | W | |
|-----------------|---|---------|-------------------------|---------|---------|---------|---------|---------|
| | 303.15K | 313.15K | 303.15K | 313.15K | 303.15K | 313.15K | 303.15K | 313.15K |
| 0.0000 | 77.3348 | 82.7316 | 0.5514 | 0.5785 | 5471 | 5471 | 3034 | 3034 |
| 0.1088 | 77.0941 | 82.5212 | 0.5505 | 0.5777 | 5328 | 5302 | 2966 | 2953 |
| 0.2156 | 77.3657 | 82.7871 | 0.5515 | 0.5787 | 5203 | 5163 | 2906 | 2886 |
| 0.3202 | 77.8006 | 83.4703 | 0.5530 | 0.5811 | 5090 | 5048 | 2851 | 2831 |
| 0.4229 | 78.4493 | 84.4317 | 0.5553 | 0.5844 | 4991 | 4945 | 2804 | 2782 |
| 0.5237 | 79.4427 | 85.6923 | 0.5588 | 0.5887 | 4909 | 4862 | 2764 | 2742 |
| 0.6225 | 80.8015 | 87.4628 | 0.5636 | 0.5948 | 4858 | 4806 | 2739 | 2714 |
| 0.7195 | 82.7064 | 89.4942 | 0.5702 | 0.6017 | 4821 | 4770 | 2722 | 2697 |
| 0.8147 | 84.8780 | 91.8072 | 0.5777 | 0.6094 | 4794 | 4749 | 2709 | 2687 |
| 0.9082 | 87.3370 | 94.8627 | 0.5860 | 0.6194 | 4779 | 4750 | 2701 | 2687 |
| 1.0000 | 90.3739 | 98.6213 | 0.5961 | 0.6316 | 4774 | 4785 | 2699 | 2704 |

Table 3: Variation of V_m^E , $\Delta\beta_{ad}$, $\Delta\eta_{cp}$, L_r^E Temperatures 303.15K & 313.15K.

| Mole Fraction X | $V_m^E \text{ Cm}^3 \text{ mol}^{-1}$ | | $\Delta\beta_{ad} 10^{10} \text{m}^2 \text{ N}^{-1}$ | | $\Delta\eta_{cp}$ | | $L_r^E 10^{-10} \text{m}$ | |
|-----------------|---------------------------------------|---------|--|---------|-------------------|---------|---------------------------|---------|
| | 303.15K | 313.15K | 303.15K | 313.15K | 303.15K | 313.15K | 303.15K | 313.15K |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1088 | -1.4200 | -1.9300 | -1.6600 | -1.9400 | 0.0343 | 0.0256 | -0.0057 | -0.0065 |
| 0.2156 | -2.4700 | -3.3000 | -2.7800 | -3.3700 | 0.0612 | 0.0531 | -0.0095 | -0.0113 |
| 0.3202 | -3.3100 | -4.1800 | -3.7100 | -4.3500 | 0.0872 | 0.0760 | -0.0127 | -0.0144 |
| 0.4229 | -3.8800 | -4.8500 | -4.4000 | -5.0200 | 0.1071 | 0.0938 | -0.0150 | -0.0166 |
| 0.5237 | -4.1400 | -5.1400 | -4.7200 | -5.3600 | 0.1164 | 0.1019 | -0.0160 | -0.0176 |
| 0.6225 | -3.8200 | -4.9100 | -4.6500 | -5.1600 | 0.1057 | 0.0925 | -0.0156 | -0.0168 |
| 0.7195 | -3.1800 | -4.3100 | -4.0100 | -4.6700 | 0.0864 | 0.0750 | -0.0133 | -0.0150 |
| 0.8147 | -2.3500 | -3.4200 | -3.0800 | -3.8700 | 0.0640 | 0.0544 | -0.0102 | -0.0124 |
| 0.9082 | -1.2900 | -2.0500 | -1.8400 | -2.3000 | 0.0364 | 0.0288 | -0.0060 | -0.0073 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

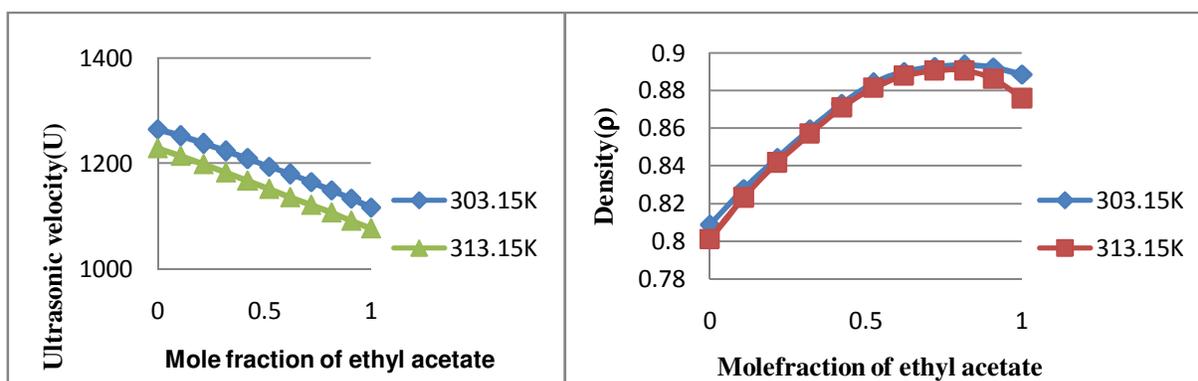


Fig.1. A. Variation of ultrasonic velocity with mole fraction of ethyl acetate for ethyl acetate + n-pentanol system. **B.** Variation of Density with mole fraction of ethyl acetate + n-Pentanol system.

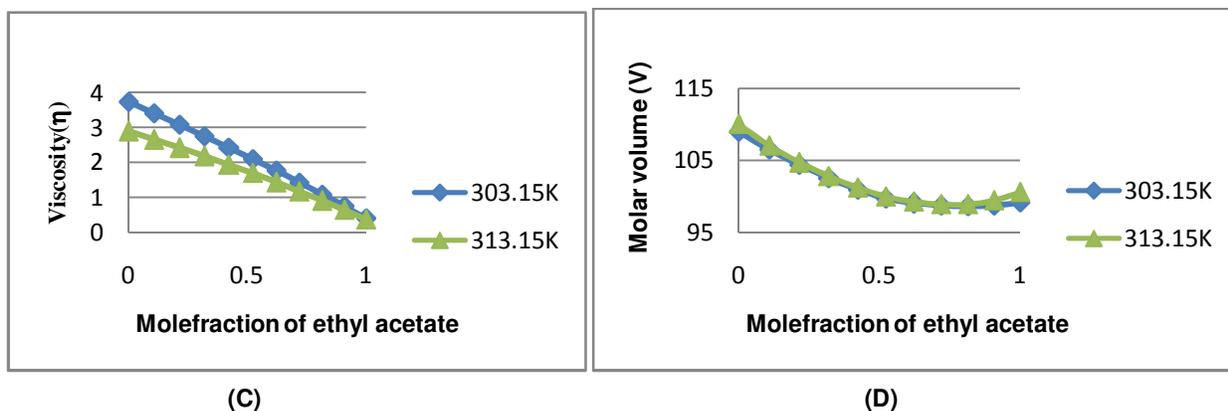
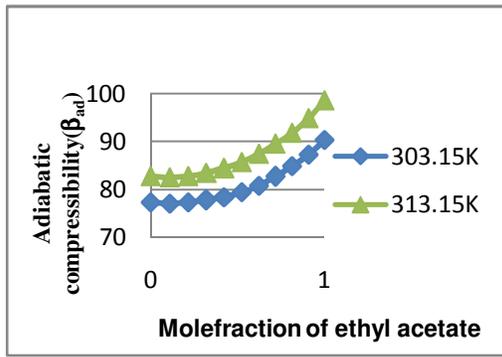


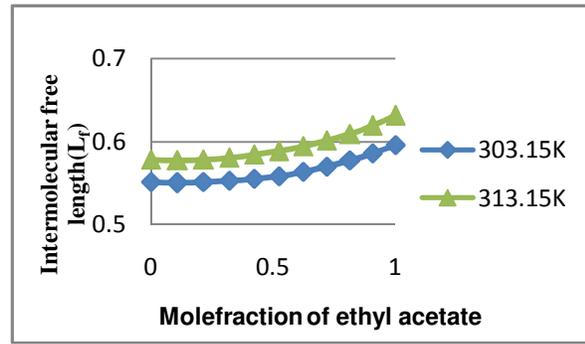
Fig. 2.(C) Variation of viscosity with mole fraction of ethyl acetate for ethyl acetate + n-pentanol system. **(D)** Variation of molar volume with mole fraction of ethyl acetate for ethyl acetate + n-pentanol system.

The results indicate that there is a volume contraction in mixing. The V^E values become more and more negative as the temperature is increased. The broad negative V^E is observed at about 0.52 mole fraction of ethyl acetate. Plotting of Variation of adiabatic compressibility (β_{ad}) and the deviation in adiabatic compressibility ($\Delta\beta_{ad}$) are shown in Fig. 3(A) and Fig. 5(B). It can be seen that the deviation in adiabatic compressibility ($\Delta\beta_{ad}$) is negative over the entire composition range reaching broad

minimum at about 0.52 mole fractions. Variation of intermolecular free length (L_r) and excess intermolecular free length (L_r^E) is shown in Fig. 3(B) and Fig. 6(D). These curves indicated that the intermolecular free length varies non-linearly with mole fraction and increases slightly with increase in temperature. The variation of Rao's constant (R) and Wada's Constant (W)[18-20] is depicted in Figs. 4(C) and 4(D).

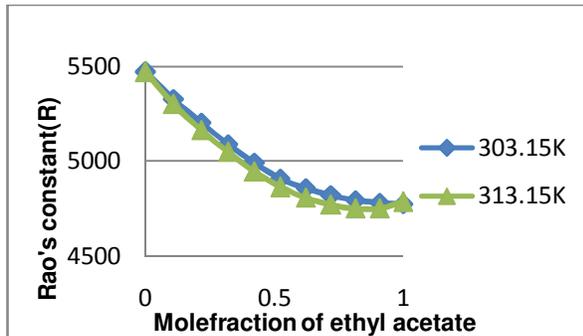


(A)

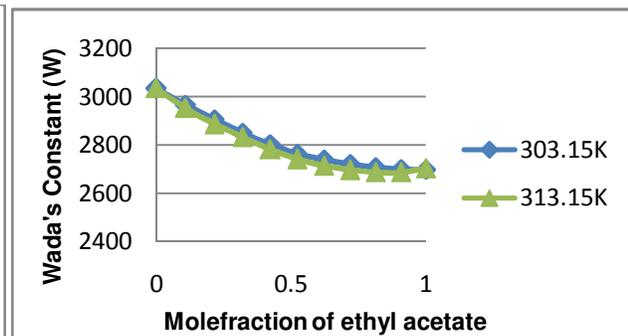


(B)

Fig. 3 (A) Variation of adiabatic compressibility with mole fraction of ethyl acetate for ethyl acetate + n-pentanol system, (B) Variation of intermolecular free length with mole fraction of ethyl acetate for ethyl acetate + n-pentanol system.

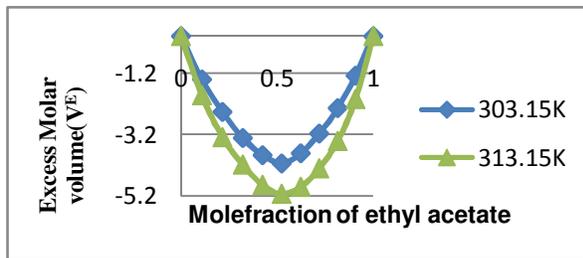


(A)

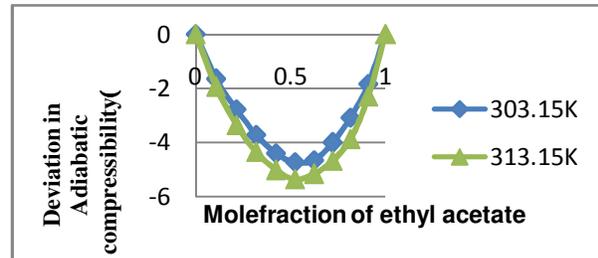


(B)

Fig. 4 (A) Variation of Rao's constant with mole fraction of ethyl acetate for ethyl acetate + n-pentanol system, (B) Variation of Wada's constant with mole fraction of ethyl acetate for ethyl acetate + n-pentanol system.

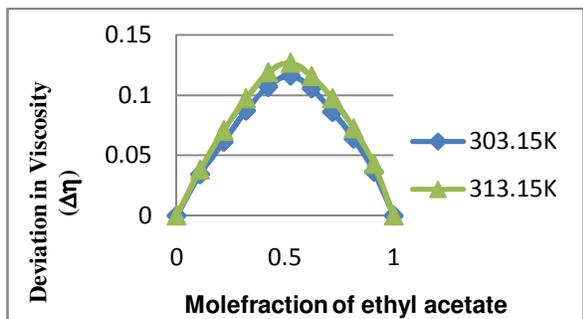


(A)

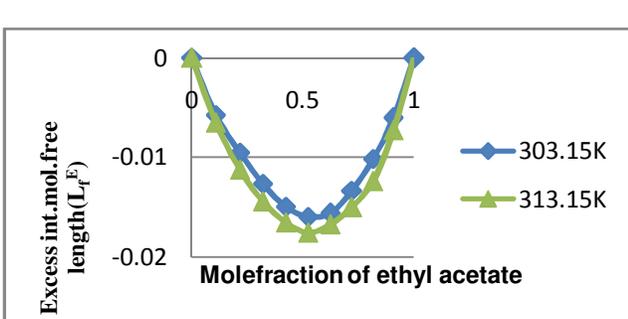


(B)

Fig. 5 (A) Variation of excess molar volume with mole fraction of ethyl acetate for ethyl acetate + n-pentanol system (B) Variation of deviation in adiabatic compressibility with mole fraction of ethyl acetate for ethyl acetate + n-pentanol system.



(C)



(D)

Fig.6 (C) Variation of deviation in viscosity with mole fraction of ethyl acetate for ethyl acetate + n-pentanol system (D) Variation of excess inter molecular free length with mole fraction of ethyl acetate for ethyl acetate + n-pentanol system.

From the Figs, there is a linearity of these constants at all the temperatures. These results are favoring the dipole-dipole interactions between unlike molecules in binary mixtures.

The excess values ($V_m^E, L_f^E, \Delta\beta_{ad}$ and $\Delta\eta$) are fitted in to an empirical equation of the form

$$A^E = X_1 X_2 [A + B(X_1 - X_2) + C(X_1 - X_2)^2]$$

Where A^E is the excess parameter, X_1 and X_2 is the mole fraction of the two components. The coefficients A, B and C evaluated from linear least square method are

given in tables. The standard deviations σ of (A^E) are evaluated by the following relation.

$$\sigma(A^E) = \Sigma(A_{exp}^E - A_{eq}^E) / (m-n)^{1/2}$$

Where m is number of experimental data and n is the number of coefficients.

The results of the excess values indicate that the experimental and theoretical values are in good correlation (Tables 4-7).

Table 4: Variation of molar volumes at 303.15K AND 313.15K.

| Mole fraction X | Temperature 303.15K A = 0.1115 B = -1.0615 C = -1.1985 $\sigma = 0.1325$ | | Temperature 313.15K A = -0.3320 B = 1.1215 C = -2.1125 $\sigma = 0.1115$ | |
|-----------------|--|----------------------------|--|----------------------------|
| | (V_m^E) | (V_m^E) _{cal} | V_m^E | (V_m^E) _{cal} |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1088 | -1.4200 | -1.4200 | -1.9300 | -1.9300 |
| 0.2156 | -2.4700 | -2.4755 | -3.3000 | -3.3150 |
| 0.3202 | -3.3100 | -3.3155 | -4.1800 | -4.1855 |
| 0.4229 | -3.8800 | -3.8750 | -4.8500 | -4.8525 |
| 0.5237 | -4.1400 | -4.1400 | -5.1400 | -5.1400 |
| 0.6225 | -3.8200 | -3.8225 | -4.9100 | -4.9120 |
| 0.7195 | -3.1800 | -3.1835 | -4.3100 | -4.3250 |
| 0.8147 | -2.3500 | -2.3400 | -3.4200 | -3.4160 |
| 0.9082 | -1.2900 | -1.2900 | -2.0500 | -2.0500 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

Table 5: Deviation in adiabatic compressibility, a, b, c and σ values.

| Mole fraction X | Temperature 303.15K A = -5.3541 B = 1.5236 C = -1.6584 $\sigma = 0.0256$ | | Temperature 313.15K A = -2.1625 B = 0.2514 C = -3.254 $\sigma = 0.15001$ | |
|-----------------|--|---------------------------------------|--|---------------------------------------|
| | $\Delta\beta_{ad}$ | ($\Delta\beta_{ad}$) _{cal} | $\Delta\beta_{ad}$ | ($\Delta\beta_{ad}$) _{cal} |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1088 | -1.6600 | -1.6600 | -1.9400 | -1.9400 |
| 0.2156 | -2.7800 | -2.7825 | -3.3700 | -3.3790 |
| 0.3202 | -3.7100 | -3.7280 | -4.3500 | -4.3580 |
| 0.4229 | -4.4000 | -4.4150 | -5.0200 | -5.0150 |
| 0.5237 | -4.7200 | -4.7200 | -5.3600 | -5.3600 |
| 0.6225 | -4.6500 | -4.6585 | -5.1600 | -5.1810 |
| 0.7195 | -4.0100 | -4.0190 | -4.6700 | -4.6690 |
| 0.8147 | -3.0800 | -3.0885 | -3.8700 | -3.8650 |
| 0.9082 | -1.8400 | -1.8400 | -2.3000 | -2.3000 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

To further substantiate the presence of interactions it is pivotal to examine the excess parameters like free volume, internal pressure and enthalpy [18]. Variation of free Volume (V_f), Internal pressure (π) and Enthalpy shown in Fig 7(A),(B) & (C) respectively. The decrease in free volume, Enthalpy and increase in internal pressure suggests the close packing of the molecules inside which was suggested by Jacobson [19-22].

Excess values of Internal Pressure and Enthalpy (π^E & H^E) are shown in Figs. 8(B) and 9(D) shows that first the graph increase, attain maximum value at 0.5 and 0.6 mole fraction of ethyl acetate respectively. Data presented in Tables [from 8 to 13] as well as Figs. 7(B) & (C) also indicate clearly that increase in temperature cause variation in the experimental values of all the excess thermodynamic.

Table 6: Deviation in Viscosity at 303.15K & 313.15K.

| Mole fraction X | Temperature 303.15K A = 0.2299 B = - 0.2272 C = - 0.0547 $\sigma = 0.0521$ | | Temperature 313.15K A = 0.1229 B = -0.3783 C = -0.1367 $\sigma = 0.0021$ | |
|-----------------|--|----------------------|--|----------------------|
| | $\Delta\eta$ | $(\Delta\eta)_{cal}$ | $\Delta\eta$ | $(\Delta\eta)_{cal}$ |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1088 | 0.0343 | 0.0343 | 0.0256 | 0.0256 |
| 0.2156 | 0.0612 | 0.0619 | 0.0531 | 0.0522 |
| 0.3202 | 0.0872 | 0.0873 | 0.0760 | 0.0772 |
| 0.4229 | 0.1071 | 0.1080 | 0.0938 | 0.0945 |
| 0.5237 | 0.1164 | 0.1164 | 0.1019 | 0.1019 |
| 0.6225 | 0.1057 | 0.1059 | 0.0925 | 0.0932 |
| 0.7195 | 0.0864 | 0.0855 | 0.0750 | 0.0762 |
| 0.8147 | 0.0640 | 0.0655 | 0.0544 | 0.0556 |
| 0.9082 | 0.0364 | 0.0364 | 0.0288 | 0.0288 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

Table 7: Excess Intermolecular Free Length at 303.15K and 313.15K.

| Mole fraction X | TEMPERATURE 303.15K A= 0.1847 B= - 0.2125 C= - 0.0312 $\sigma = 0.0015$ | | TEMPERATURE 313.15K A= 0.0545 B= -0.0401 C= 0.0755 $\sigma = 0.0013$ | |
|-----------------|---|-----------------|--|-----------------|
| | L_f^E | $(L_f^E)_{cal}$ | L_f^E | $(L_f^E)_{cal}$ |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1088 | -0.0057 | -0.0057 | -0.0065 | -0.0065 |
| 0.2156 | -0.0095 | -0.0086 | -0.0113 | -0.0118 |
| 0.3202 | -0.0127 | -0.0119 | -0.0144 | -0.0139 |
| 0.4229 | -0.0150 | -0.0158 | -0.0166 | -0.0162 |
| 0.5237 | -0.0160 | -0.0160 | -0.0176 | -0.0176 |
| 0.6225 | -0.0156 | -0.0166 | -0.0168 | -0.0164 |
| 0.7195 | -0.0133 | -0.0139 | -0.0150 | -0.0152 |
| 0.8147 | -0.0102 | -0.0111 | -0.0124 | -0.0128 |
| 0.9082 | -0.0060 | -0.0060 | -0.0073 | -0.0073 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

Table 8: Free Volume, Internal Pressure and Enthalpy at 303.15k and 313.15k.

| Mole Fraction X | Temperature 303.15K | | | Temperature 313.15K | | |
|-----------------|--|-------------------------|----------------------|--|-------------------------|----------------------|
| | V_f $\text{Cm}^3 \text{mol}^{-1}$ | π N/m^2 | H J/mole | V_f $\text{Cm}^3 \text{mol}^{-1}$ | π N/m^2 | H J/mole |
| 0.0000 | 1.8442 | 2644.16 | 288.22 | 2.5897 | 2346.03 | 258.21 |
| 0.1088 | 2.0854 | 2577.43 | 274.52 | 2.9103 | 2297.90 | 246.11 |
| 0.2156 | 2.3857 | 2497.37 | 260.75 | 3.2973 | 2237.48 | 234.32 |
| 0.3202 | 2.7670 | 2405.76 | 246.68 | 3.7905 | 2161.72 | 222.34 |
| 0.4229 | 3.2748 | 2298.04 | 232.01 | 4.4363 | 2073.38 | 209.85 |
| 0.5237 | 3.9881 | 2169.92 | 216.35 | 5.3428 | 1964.91 | 196.43 |
| 0.6225 | 5.1013 | 2007.75 | 198.87 | 6.7387 | 1827.21 | 181.38 |
| 0.7195 | 6.9075 | 1818.65 | 179.57 | 8.9973 | 1662.92 | 164.54 |
| 0.8147 | 10.1821 | 1599.17 | 157.73 | 12.9938 | 1471.27 | 145.56 |
| 0.9082 | 17.4947 | 1333.92 | 131.75 | 21.4900 | 1240.06 | 123.29 |
| 1.0000 | 42.9102 | 986.54 | 97.82 | 47.2383 | 946.24 | 95.20 |

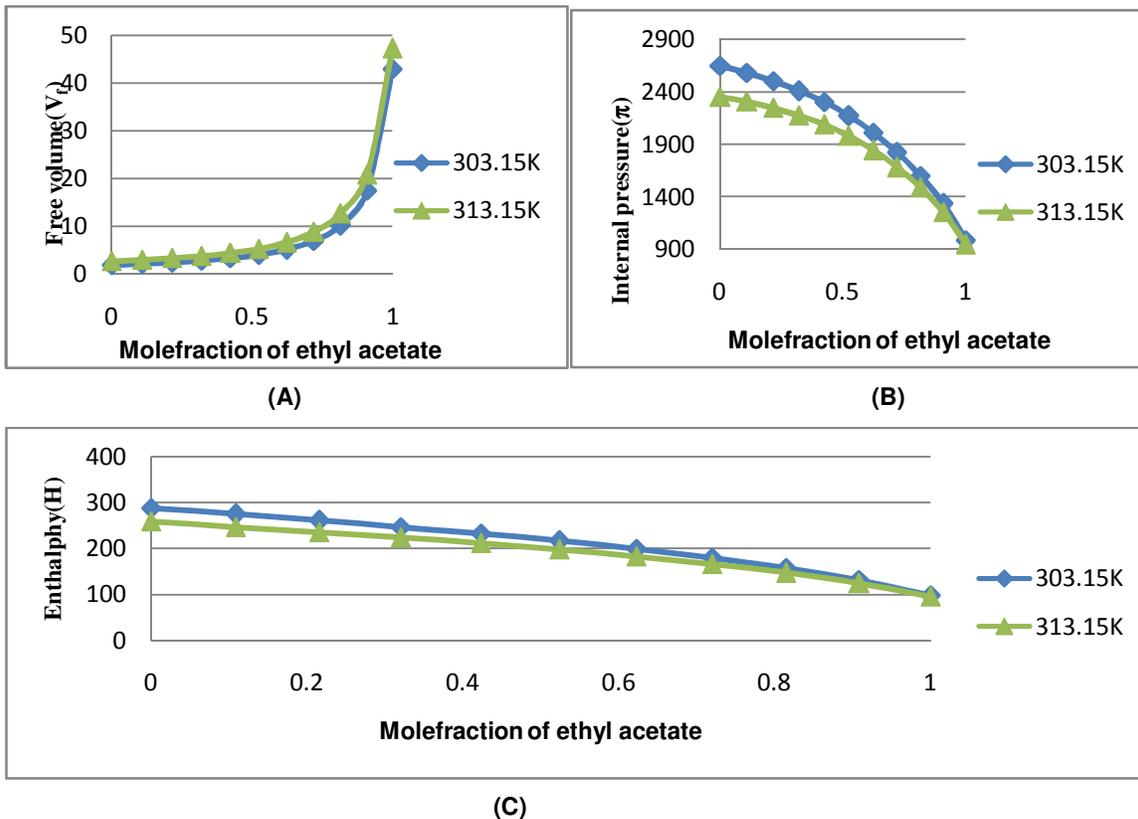


Fig. 7. (A) Variation of free volume with mole fraction of ethyl acetate for ethyl acetate + n-pentanol system, (B) Variation of internal pressure with mole fraction of ethyl acetate for ethyl acetate + n-pentanol system (C) Variation of enthalpy with mole fraction of ethyl acetate for ethyl acetate + n-pentanol system.

The excess values of π^E and H^E show positive, thus suggesting strong interaction between the mixing components of molecules. The variation of excess internal pressure (π^E) is entirely positive. The positive values of the excess enthalpies (H^E) indicate that the breaking of the interactions existing in the pure compounds, especially the strong interactions which is the main source of the energetic behavior. Variations in Excess free volume and Excess Gibbs free energy shown in Fig. 8(A) & 9(C) respectively. We observed that G^E is positive which indicates of strong molecular

interaction [23]. Several attempts have been made by various workers [24-28] relate G^E to chemical interaction. Hence a conclusion can be drawn that chemical forces are dominating over the physical forces in the above system [29].

The ΔG^E have local maxima at mole fraction about 0.5 for the system due to the interactions of the alcohol molecules. The negative values of excess free volume, excess molar volume, excess intermolecular free length, deviation in adiabatic compressibility and positive values of excess internal pressure, excess enthalpy excess,

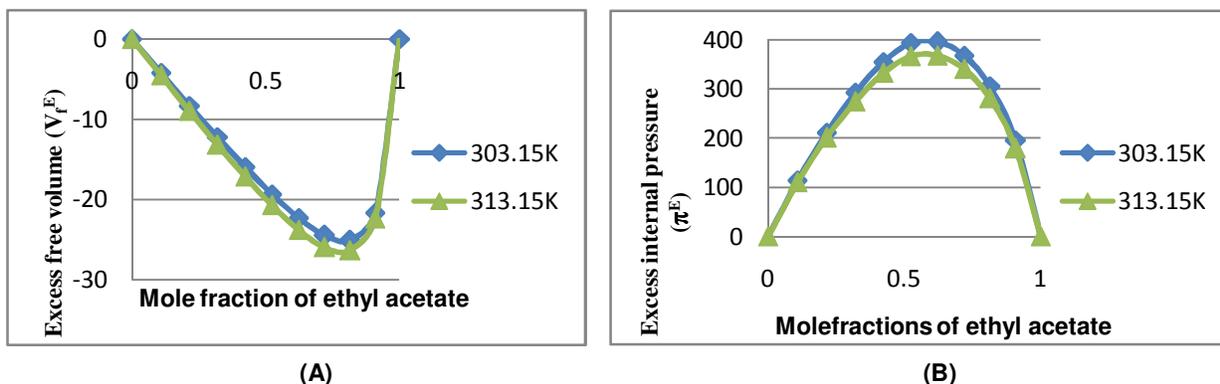
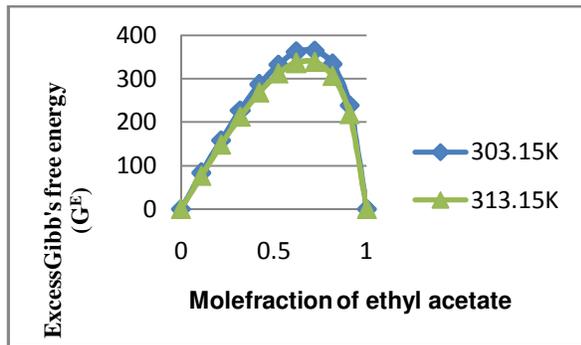
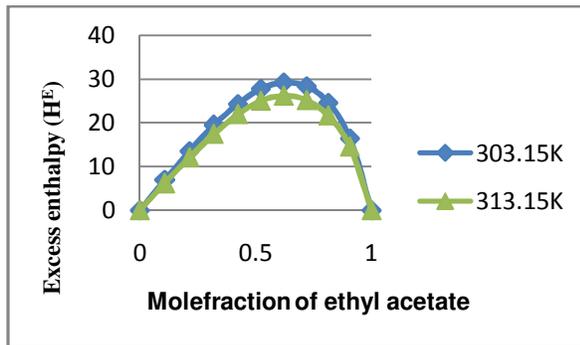


Fig. 8 (A) Variation of excess free volume with mole fraction of ethyl acetate for ethyl acetate + n-pentanol system (B) Variation of excess internal pressure with mole fraction of ethyl acetate for ethyl acetate + n-pentanol system.



(C)



(D)

Fig. 9 (C) Variation of excess Gibb's free energy with mole fraction of ethyl acetate for ethyl acetate + n-pentanol system **(D)** Variation of excess enthalpy with mole fraction of ethyl acetate for ethyl acetate + n-pentanol system.

Gibbs free energy of activation and deviation in viscosity hint to the presence of strong dipole - dipole interactions between the component molecules in the liquid mixture studied and the inherent nature of ethyl acetate

predominant the existing strong interactions. The results of the values indicate that the experimental and theoretical values are in good correlation (Tables 8-13).

Table 9: Variation of excess free volume, excess internal pressure excess enthalpy and excess Gibb's free energy at 303.15K AND 313.15K.

| Mole Fraction X | TEMPERATURE – 303.15K | | | | TEMPERATURE 313.15K | | | |
|-----------------|--|-----------------------------|-----------------|------------------|--|-----------------------------|-----------------|------------------|
| | V_f^E Cm ³ mol ⁻¹ | π^E N/m ² | H^E J/mole | G^E Cal/mol | V_f^E Cm ³ mol ⁻¹ | π^E N/m ² | H^E J/mole | G^E Cal/mol |
| 0.0000 | 0.0000 | 0.00 | 0.00 | 0.00 | 0.0000 | 0.00 | 0.00 | 0.00 |
| 0.1088 | -4.2288 | 113.70 | 7.03 | 82.66 | -4.5394 | 104.23 | 5.65 | 73.12 |
| 0.2156 | -8.3115 | 210.56 | 13.58 | 158.61 | -8.9176 | 193.22 | 11.25 | 142.70 |
| 0.3202 | -12.2286 | 292.46 | 19.44 | 227.19 | -13.0979 | 263.97 | 16.34 | 206.08 |
| 0.4229 | -15.9371 | 354.92 | 24.31 | 286.33 | -17.0362 | 319.35 | 20.58 | 260.13 |
| 0.5237 | -19.3604 | 393.78 | 27.84 | 332.79 | -20.6272 | 351.88 | 23.58 | 302.15 |
| 0.6225 | -22.3062 | 395.44 | 29.18 | 360.89 | -23.6444 | 352.54 | 24.64 | 325.64 |
| 0.7195 | -24.4836 | 367.15 | 28.34 | 364.71 | -25.7170 | 324.03 | 23.62 | 325.88 |
| 0.8147 | -25.1193 | 305.50 | 24.63 | 333.05 | -25.9720 | 265.68 | 20.16 | 293.26 |
| 0.9082 | -21.6458 | 195.21 | 16.45 | 238.90 | -21.6498 | 165.32 | 13.13 | 204.50 |
| 1.0000 | 0.0000 | 0.00 | 0.00 | 0.00 | 0.0000 | 0.00 | 0.00 | 0.00 |

Table 10: Excess free volumes at 303.15K & 313.15K.

| Mole fraction X | Temperature 303.15K A = -10.4425 B = -10.4125 C = -71235 $\sigma = 0.4356$ | | Temperature 313.15K A = -18.4253 B = -16.5266 C = -6.1256 $\sigma = 0.7856$ | |
|-----------------|--|-----------------|---|-----------------|
| | V_f^E | $(V_f^E)_{cal}$ | V_f^E | $(V_f^E)_{cal}$ |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1088 | -4.2288 | -4.2288 | -4.5394 | -4.5394 |
| 0.2156 | -8.3115 | -8.3563 | -8.9176 | -8.9456 |
| 0.3202 | -12.2286 | -12.2458 | -13.0979 | -13.1245 |
| 0.4229 | -15.9371 | -15.9758 | -17.0362 | -17.1236 |
| 0.5237 | -19.3604 | -19.3604 | -20.6272 | -20.6272 |
| 0.6225 | -22.3062 | -22.3785 | -23.6444 | -23.6231 |
| 0.7195 | -24.4836 | -24.4012 | -25.7170 | -25.7125 |
| 0.8147 | -25.1193 | -25.4521 | -25.9720 | -25.9452 |
| 0.9082 | -21.6458 | -21.6458 | -21.6498 | -21.6498 |
| 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

The experimental and theoretical values using the relations of Nomoto and Van Dael ideal mixing for Ethyl acetate + n-Pentanol are given in Tables 14 and Fig 10. The table and graph replicates that there is good agreement between experimental and theoretical values calculated by VanDael ideal mixing and Nomoto relations. Here Nomoto's relation provides the best

result than the result of ideal mixing relation which is in good agreement with the conclusions drawn by others [29-32]. The ratio U^2_{exp}/U^2_{imx} is used as an important tool to measure the non-ideality in the mixtures, especially in these cases where the properties other than sound velocity are not known.

Table 11: Excess Internal Pressures at 303.15K & 313.15K.

| Mole fraction X | Temperature 303.15K A = -11.2356 B = -30.7896 C = 10.8532 $\sigma = 0.6856$ | | Temperature 313.15K A = 12.5632 B = 21.7562 C = -32.4523 $\sigma = 0.7856$ | |
|-----------------|---|-----------------|--|-----------------|
| | π^E | $(\pi^E)_{cal}$ | π^E | $(\pi^E)_{cal}$ |
| 0.0000 | 0.00 | 0.00 | 0.00 | 0.00 |
| 0.1088 | 113.70 | 113.70 | 104.23 | 104.23 |
| 0.2156 | 210.56 | 210.33 | 193.22 | 193.56 |
| 0.3202 | 292.46 | 292.52 | 263.97 | 263.24 |
| 0.4229 | 354.92 | 354.45 | 319.35 | 319.87 |
| 0.5237 | 393.78 | 393.78 | 351.88 | 351.88 |
| 0.6225 | 395.44 | 395.24 | 352.54 | 352.65 |
| 0.7195 | 367.15 | 367.02 | 324.03 | 324.56 |
| 0.8147 | 305.50 | 305.75 | 265.68 | 265.35 |
| 0.9082 | 195.21 | 195.21 | 165.32 | 165.32 |
| 1.0000 | 0.00 | 0.00 | 0.00 | 0.00 |

Table 12: Excess Enthalpy at 303.15K & 313.15K.

| Mole fraction X | Temperature 303.15K A = -1.9856 B = 12.4563 C = -8.4523 $\sigma = 0.9965$ | | Temperature 313.15K A = -2.0012 B = -13.1235 C = 6.3652 $\sigma = 0.8998$ | |
|-----------------|---|---------------|---|---------------|
| | H^E | $(H^E)_{cal}$ | H^E | $(H^E)_{cal}$ |
| 0.0000 | 0.00 | 0.00 | 0.00 | 0.00 |
| 0.1088 | 7.03 | 7.03 | 5.65 | 5.65 |
| 0.2156 | 13.58 | 13.35 | 11.25 | 11.65 |
| 0.3202 | 19.44 | 19.56 | 16.34 | 16.55 |
| 0.4229 | 24.31 | 24.27 | 20.58 | 20.96 |
| 0.5237 | 27.84 | 27.84 | 23.58 | 23.58 |
| 0.6225 | 29.18 | 29.38 | 24.64 | 24.87 |
| 0.7195 | 28.34 | 28.75 | 23.62 | 23.45 |
| 0.8147 | 24.63 | 24.46 | 20.16 | 20.38 |
| 0.9082 | 16.45 | 16.45 | 13.13 | 13.13 |
| 1.0000 | 0.00 | 0.00 | 0.00 | 0.00 |

Table 13: Excess Gibb's Free Energy at 303.15K & 313.15K.

| Mole fraction X | TEMPERATURE 303.15K A = - 40.2006 B = -20.3126 C = 10.4123 $\sigma = 3.4525$ | | TEMPERATURE 313.15K A = -24.3568 B = -14.1425 C = -36.7423 $\sigma = 2.0102$ | |
|-----------------|--|---------------|--|---------------|
| | G^E | $(G^E)_{cal}$ | G^E | $(G^E)_{cal}$ |
| 0.0000 | 0.00 | 0.00 | 0.00 | 0.00 |
| 0.1088 | 82.66 | 82.66 | 73.12 | 73.12 |
| 0.2156 | 158.61 | 158.45 | 142.70 | 142.58 |
| 0.3202 | 227.19 | 227.05 | 206.08 | 206.26 |
| 0.4229 | 286.33 | 286.88 | 260.13 | 260.24 |
| 0.5237 | 332.79 | 332.79 | 302.15 | 302.15 |
| 0.6225 | 360.89 | 360.586 | 325.64 | 325.38 |
| 0.7195 | 364.71 | 364.25 | 325.88 | 325.27 |
| 0.8147 | 333.05 | 333.45 | 293.26 | 293.55 |
| 0.9082 | 238.90 | 238.90 | 204.50 | 204.50 |
| 1.0000 | 0.00 | 0.00 | 0.00 | 0.00 |

Table 14: Nomoto Relation (NOM) & Vandael Vangeel Ideal Mixing Relation (VAN) at Two Temperature 303.15K AND 313.15K.

| Mole fraction X | Temperature – 303.15K | | | | | | Temperature – 313.15K | | | | | |
|-----------------|-----------------------|--------------|------------|------------|-------------|-----------------------|-----------------------|--------------|------------|------------|-------------|-----------------------|
| | U_{exp} m/s | U_{Nomoto} | U_{idmx} | % U_{No} | % U_{imx} | U^2_{exp}/U^2_{imx} | U_{exp} m/s | U_{Nomoto} | U_{idmx} | % U_{No} | % U_{imx} | U^2_{exp}/U^2_{imx} |
| 0.0000 | 1264.50 | 1264.50 | 1264.50 | 0.0000 | 0.0000 | 1.0000 | 1228.50 | 1228.50 | 1228.50 | 0.0000 | 0.0000 | 1.0000 |
| 0.1088 | 1251.94 | 1249.04 | 1245.39 | -0.2322 | -0.5239 | 1.0106 | 1213.44 | 1212.29 | 1208.69 | -0.0949 | -0.3921 | 1.0079 |
| 0.2156 | 1237.39 | 1233.77 | 1227.46 | -0.2925 | -0.8022 | 1.0162 | 1197.99 | 1196.54 | 1190.16 | -0.1208 | -0.6534 | 1.0132 |
| 0.3202 | 1222.85 | 1218.62 | 1210.62 | -0.3457 | -1.0005 | 1.0203 | 1182.41 | 1180.95 | 1172.80 | -0.1235 | -0.8123 | 1.0164 |
| 0.4229 | 1208.39 | 1203.60 | 1194.75 | -0.3959 | -1.1286 | 1.0230 | 1166.26 | 1165.50 | 1156.49 | -0.0657 | -0.8381 | 1.0170 |
| 0.5237 | 1193.37 | 1188.71 | 1179.78 | -0.3906 | -1.1389 | 1.0232 | 1150.55 | 1150.20 | 1141.13 | -0.0304 | -0.8187 | 1.0166 |
| 0.6225 | 1179.44 | 1173.93 | 1165.62 | -0.4664 | -1.1714 | 1.0238 | 1134.85 | 1135.05 | 1126.64 | 0.0179 | -0.7231 | 1.0146 |
| 0.7195 | 1163.94 | 1159.28 | 1152.21 | -0.4003 | -1.0081 | 1.0205 | 1120.13 | 1120.05 | 1112.95 | -0.0064 | -0.6406 | 1.0129 |
| 0.8147 | 1148.36 | 1144.76 | 1139.49 | -0.3135 | -0.7722 | 1.0156 | 1105.89 | 1105.20 | 1099.98 | -0.0623 | -0.5342 | 1.0108 |
| 0.9082 | 1132.90 | 1130.35 | 1127.40 | -0.2250 | -0.4853 | 1.0098 | 1090.62 | 1090.49 | 1087.68 | -0.0120 | -0.2697 | 1.0054 |
| 1.0000 | 1115.90 | 1115.90 | 1115.90 | 0.0000 | 0.0000 | 1.0000 | 1076.00 | 1076.00 | 1076.00 | 0.0000 | 0.0000 | 1.0000 |

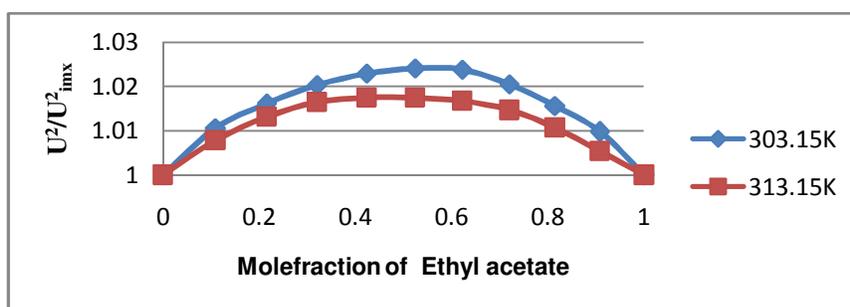


Fig. 10. Variation of U^2/U^2_{imx} with mole fraction of ethyl acetate for ethyl acetate + n-pentanol system.

CONCLUSIONS

The present study provides a comprehensive understanding of dipole-dipole interactions in binary liquid mixture taken. Data on the excess parameters has been used for understanding the structural deviations and molecular interactions between unlike molecules and they are fitted into Redlich – Kister equation to test the quality of the experimental values. Estimated coefficients and standard deviation values are also presented for better understanding the nature of the binary system.

FUTURE SCOPE

Taking this study as a reference, thermodynamic properties of many other binary mixtures can be studied at different temperatures that can help in developing new theoretical models which can help many industries in big way.

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REFERENCES

- [1]. Marekha, B. A., Bria, M., Moreau, M., De Waele, I., Miannay, F. A., Smortsova, Y., ... & Idrissi, A. (2015). Intermolecular interactions in mixtures of 1-n-butyl-3-methylimidazolium acetate and water: Insights from IR, Raman, NMR spectroscopy and quantum chemistry calculations. *Journal of Molecular Liquids*, 210, 227-237.
- [2]. Zarrougui, R., Dhahbi, M., & Lemordant, D. (2015). Transport and thermodynamic properties of ethylammonium nitrate–water binary mixtures: effect of temperature and composition. *Journal of Solution Chemistry*, 44(3-4), 686-702.
- [3]. Cao, Q., Lu, X., Wu, X., Guo, Y., Xu, L., & Fang, W. (2015). Density, viscosity, and conductivity of binary mixtures of the ionic liquid N-(2-Hydroxyethyl) piperazinium propionate with water, methanol, or ethanol. *Journal of Chemical & Engineering Data*, 60(3), 455-463.
- [4]. Bagheri, A., & Mirbakhshi, S. A. (2016). Study of the surface properties and surface concentration of ionic liquid–alcohol mixtures. *Physics and Chemistry of Liquids*, 54(4), 529-541.
- [5]. Belmonte, D., Gatti, C., Ottonello, G., Richet, P., & Vetuschi Zuccolini, M. (2016). Ab initio thermodynamic and thermophysical properties of sodium metasilicate, Na_2SiO_3 , and their electron-density and electron-pair-density counterparts. *The Journal of Physical Chemistry A*, 120(44), 8881-8895.
- [6]. Masoumeh Rajati Qazvini, Leila Pishkar and Dariush Robati (2016). Theoretical study of structure thermodynamic properties Caffeic acid as powerful antioxidants. *Biological Forum – An International Journal*, Vol. 8(1): 101-107
- [7]. Budeanu, M. M., & Dumitrescu, V. (2017). Densities and viscosities for binary mixtures of n-heptane with alcohols at different temperatures. *J. Serb. Chem. Soc.*, 82(7-8), 891-903.
- [8]. Bittencourt, S. S., Hoga, H. E., Torres, R. B., & d'Angelo, J. V. H. (2019). Thermodynamic properties of binary mixtures of

- n-butylammonium-based ionic liquids with ethanol at T=(293.15–313.15) K. *Journal of Thermal Analysis and Calorimetry*, 135(4), 2519-2539.
- [9]. Raju, M., Banuti, D. T., Ma, P. C., & Ihme, M. (2017). Widom lines in binary mixtures of supercritical fluids. *Scientific reports*, 7(1), 3027.
- [10]. Regiane Silva Pinheiro Francisca, Maria Rodrigues Mesquita, Filipe Xavier Feitosa, Hosiberto Batista de Sant'Ana, Rílvia Saraiva de Santiago-Aguiar (2018). Density, Viscosity And Excess Properties Of Binary Mixtures Of Protic Ionic Liquid (2-Hdeaf, 2-Hdeaa) + Water At Different Temperatures. *Braz. J. Chem. Eng. Vol. 35* no. 2
- [11]. Jyotsna Gupta, Renu Nair (Ahuja) and K. Dwivedi (2015). Ternary Complexes of Cd(II) and Gd(III) Involving Biologically Important Ligands. *International Journal of Theoretical & Applied Sciences*, 7(1): 22-34.
- [12]. Sprenger, K. G., Jaeger, V. W., & Pfaendner, J. (2015). The general AMBER force field (GAFF) can accurately predict thermodynamic and transport properties of many ionic liquids. *The Journal of Physical Chemistry B*, 119(18), 5882-5895.
- [13]. Tian, S., Ren, S., Hou, Y., Wu, W., & Peng, W. (2013). Densities, viscosities and excess properties of binary mixtures of 1, 1, 3, 3-Tetramethylguanidinium lactate+ water at T=(303.15 to 328.15) K. *Journal of Chemical & Engineering Data*, 58(7), 1885-1892.
- [14]. P. Anila, K. Ryapa Reddy, G. Srinivasa Rao, P.V.S. Sai Ram, D. Ramachandran, C. Rambabu (2015). Phase equilibrium and excess Gibbs energy functions of acetophenone with 1,1,2-trichloroethene and cyclohexane binary mixtures by using NRTL, UNIQUAC, UNIFAC and VANLAAR models at a local atmospheric pressure of 95.3 kPa. *Journal of Molecular Liquids*. Vol. 202, Pages 107-114.
- [15]. Clough, M.T., C.R. Crick, J. Grasvik, P.A. Hunt and H. Niedermeyer (2015). A physicochemical investigation of ionic liquid mixtures. *Chem. Sci.*, 6: 1101-1114.
- [16]. Gençaslan, M., & Keskin, M. (2016). Investigation of critical lines and global phase behavior of unequal size of molecules in binary gas–liquid mixtures in the combined pressure–temperature–concentration planes around the van Laar point. *Physica A: Statistical Mechanics and its Applications*, 457, 454-464.
- [17]. Mishra, M., U.N. Dash and N. Swain (2016). Acoustical and thermo dynamical studies of binary liquid mixtures of Tri-n-Butyl Phosphate and Benzene at different temperatures. *J. Chem. Pharm. Res.*, 8: 909-914.
- [18]. Ono, T., Horikawa, K., Maeda, Y., Ota, M., Sato, Y., & Inomata, H. (2016). Dynamic properties of methanol–water mixtures at the temperatures up to 476.2 K and at high pressures via molecular dynamics simulation. *Fluid Phase Equilibria*, 420, 30-35.
- [19]. Jahan, Aklima & Alam, Dr. Md. Ashraf & Awual, Rabiul & Akhtar, Shamim. (2019). Volumetric and Acoustic Properties for Binary Mixtures of N,N-Dimethylformamide with 2-Butanol and 2-Pentanol at Temperatures between 298.15 K and 318.15 K. *American Journal of Chemistry*, Vol. 9(1): PP 1-12
- [20]. Salhi, H., Babu, S., Al-Arfaj, A. A., Alkhaldi, M. A., Alzamel, N. O., Akhtar, S., & Querfelli, N. (2016). The reduced Redlich-Kister equations for correlating excess properties of 1, 2-dimethoxyethane+ water binary mixtures at temperatures from 303.15 K to 323.15 K. *Rasayan J Chem*, 9, 864-877.
- [21]. Sandhya, M. S., Govinda, V., Bahadur, I., & Venkateswarlu, P. (2017). Nature of the molecular interaction between 1-ethyl-3-methylimidazolium methylsulfate ionic liquid with higher chain alcohol through binary mixtures containing thermophysical properties. *Journal of Molecular Liquids*, 240, 613-621.
- [22]. Majid Taghizadeh, Saber Sheikhv and Amiri (2017). Experimental measurements and modelling of the solvent activity and surface tension of binary mixtures of poly(vinyl pyrrolidone) in water and ethanol. *J. Serb. Chem. Soc.* 82 (4) 427–435.
- [23]. H. Kaur and A. Singla (2009). Comparative study of stability constants and thermodynamic properties of complexation of Aspirin and Paracetamol with divalent metal ions by potentiometry. *International Journal of Theoretical & Applied Sciences*, 2(1): 114-117.
- [24]. Ranjana Singh Tomar (2016). Statistical Approach for the Study of Viscous Behaviour of Ternary Liquid System. *International Journal of Theoretical & Applied Sciences*, Special Issue-NCRTAST 8(1): 10-14.
- [25]. Xu, Y., Zhu, H., & Yang, L. (2013). Estimation of surface tension of ionic liquid–cosolvent binary mixtures by a modified hildebrand–scott equation. *Journal of Chemical & Engineering Data*, 58(8), 2260-2266.
- [26]. Venkatramana, L., Gardas, R. L., Rao, C. N., Sivakumar, K., & Reddy, K. D. (2015). A Study of the Excess Properties of Aliphatic Chlorinated Compounds with Benzylalcohol at Various Temperatures. *Journal of Solution Chemistry*, 44(2), 327-359.
- [27]. Kubíková, B., Boča, M., Mlynáriková, J., Netrieová, Z., & Vasková, Z. (2016). Critical evaluation of partial molar volumes and excess partial molar volumes of molten fluoride melts. *Journal of Thermal Analysis and Calorimetry*, 125(1), 497-508.
- [28]. Saravanakumar, K., Lavanya, T. G., & Kubendran, T. R. (2016). RETRACTED ARTICLE: Density, viscosity and speed of sound of benzaldehyde with benzene at 303.15, 308.15, and 313.15 K. *Journal of Engineering Thermophysics*, 25(1), 106-116.
- [29]. Chen, F., Yang, Z., Chen, Z., Hu, J., Chen, C., & Cai, J. (2015). Density, viscosity, speed of sound, excess property and bulk modulus of binary mixtures of γ -butyrolactone with acetonitrile, dimethyl carbonate, and tetrahydrofuran at temperatures (293.15 to 333.15) K. *Journal of Molecular Liquids*, 209, 683-692.
- [30]. Padmanaban, R., Venkatramanan, K., Girivel, S., Kasthuri, K., Usharani, A., Gayathri, A., & Vellaichamy, R. (2017). Mathematical and experimental analysis of ultrasound velocity and refractive index in binary mixtures of pharmaceutically important polymer—PEG 600. In *Recent Trends in Materials Science and Applications* (pp. 709-722). Springer, Cham.
- [31]. Ghazoyan, H. H., Grigoryan, Z. L., Gabrielyan, L. S., & Markarian, S. A. (2019). Study of thermodynamic properties of binary mixtures of propionitrile with dimethylsulfoxide (or diethylsulfoxide) at temperatures from (298.15 to 323.15) K. *Journal of Molecular Liquids*, 284, 147-156.
- [32]. Padidela, U. K., Khanna, T., & Behera, R. N. (2018). Structure, thermodynamics and diffusion in asymmetric binary mixtures: a molecular dynamics simulation study. *Physics and Chemistry of Liquids*, 56(5), 685-701.

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