

## Studying Various Thermodynamic Properties of Binary Mixture of Ethyl Acetate with Ethanol at 303.15 and 313.15 K

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**Abstract:** The intermolecular forces of liquids in a mixture show a considerable effect on the physical and chemical properties. A detailed study of the thermodynamic, transport and dielectric properties of fluids and fluid mixtures is important not only for the solution problems but also for the development of understanding of molecular motions and interactions in such systems. There is a continue need for reliable thermodynamic data of binary systems for chemical industries as the data is essential in the design of process involving chemical separation heat transfer, mass transfer and fluid flow. The present study deals with the variations of ultrasonic velocity, density, viscosity, various acoustic and thermodynamic parameters such as adiabatic compressibility, intermolecular free length, molar volume, acoustic impedance, free volume, internal pressure, enthalpy and also excess thermodynamic properties for Ethanol with ethyl acetate as function of concentration and temperature. All the excess parameters are fitted into the Redlich-Kister equation. And also to compare the ultrasonic sound velocity in Ethyl Acetate with Ethanol mixture from various theoretical relations of Nomoto and Van Dael Vangeel. These properties can be effectively utilized as a qualitative study to predict the extent of molecular interactions between the components.

**Key words:** Intermolecular forces, ultrasonic velocity, viscosity, adiabatic compressibility, nomoto, Van Dael and Vangeel

### INTRODUCTION

Properties of liquid-liquid mixtures are thermodynamically very important as part of studies of thermodynamic, acoustic and transport aspects. The intermolecular forces of liquids in a mixture show a considerable effect on the physical and chemical properties. There is continuing need for reliable thermodynamic data of binary systems for chemical industries as the data is essential in the design of process involving chemical separation, heat transfer, mass transfer and fluid flow. Fundamental thermodynamic and thermo physical properties are essential sources of information necessary for a better understanding of the non-ideal behavior of complex systems because of physical and chemical effects which are caused by molecular interactions, inter molecular forces, etc., of unlike molecules (Belmonte *et al.*, 2016; Tong *et al.*, 2016; Sandhya *et al.*, 2017; Jacome *et al.*, 2016).

The excess thermodynamic functions introduced by Scatchard in the year 1931, provided a way to represent directly the deviation of solution from ideal behavior. The difference between the thermodynamic function of mixing for a real system and the value corresponding to a

perfect solution at the same temperature, pressure and composition is called the excess thermodynamic parameters denoted by super script E. Thus, any excess parameter  $Y^E$  is given by:

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

Vander Waals and Van Laar (Gencaslan and Keskin, 2016) proposed the initial theories of binary liquid mixtures. These theories successfully explained certain excess properties in critical region of liquid mixtures. In an attempt to improve Van Laar's theory, Hildebrand and Scott (Xu *et al.*, 2013) and Scatchard (Bagheri and Mirbakhshi, 2016) used Hildebrand's concept of regular solutions to formulate a relation for excess volume.

Redlich and Kister proposed an empirical equation to predict  $Y^E$  values for binary mixtures (Salhi *et al.*, 2016):

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

Where:

$A_0, A_1$  and  $A_2$  = Constants

$X_1$  and  $X_2$  = The mole fractions of the two components

Wilson and Richardson reported near ideal behavior in the variation of ultrasonic velocity and compressibility in binary liquid mixtures containing benzene and n-butyl alcohol.

Rao found that the thermal coefficient of ultrasonic velocity in organic liquids is about three times the thermal coefficient of density (Mishra *et al.*, 2016; Singh and Sharma, 2013).  $R = U^{1/3} V$ , where R is a constant known as molar sound velocity constant or Rao's constant.

Jacobson proposed an empirical relation between ultrasonic velocity, density and intermolecular free length (Cloughr *et al.*, 2015). The literature survey on the ultrasonic studies indicates that enormous work has been carried out in binary and ternary liquid mixtures of weak and strong interacting systems and very few studies are reported with ethyl acetate as main component. Moreover, thermodynamic properties of these liquid mixtures are of interest for different branches of science and engineering and also play significant role in technological processes, biological process of living organisms and in nature. A survey of literature reveals no ultrasonic studies for the above liquid mixtures at different temperatures of 303.15 and 313.15 K. In order to have clear understanding of the molecular interactions between the component molecules, ultrasonic velocities, densities, viscosities and the ultrasonic sound velocity in binary liquid mixtures from various theoretical relations of Nomoto and Van Dael and Vangeel of Ethyl acetate+Ethanol at the temperatures of 303.15 and 313.15 K over the entire composition range have been studied.

## MATERIALS AND METHODS

The ultrasonic velocity measurements are made with the help of a single crystal ultrasonic pulse echo-interferometer. Number of pulses satisfying in phase condition is counted and separation between them is estimated in terms of the pulse repetition rate. The accuracy in velocity measurement is within +0.02%. The densities of the liquid mixture (Ethyl Acetate+Ethanol) have been determined by using a single pan electrical balance for the determination of mass of a given volume of the liquid. Weight measurements in the present study are made employing a single pan electronic balance capable of measuring up to 0.05 mg. The coefficient of viscosity has been determined as a function of composition and temperature, using the Oswald's viscometer. The accuracy of viscosity measurement is +0.001 cp. 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 ( $\sigma$ ). The excess volumes of mixing have been evaluated both as a function of composition and temperature to examine the possibility of structural adjustment. The closer packing of molecules due to the dipole-dipole interactions between hetero molecules is bound to have greater influence on the overall compressibility of the systems.

Ethyl acetate+ethanol, system has been chosen and studied its excess properties at the temperatures of 303.15 and 313.15 K over the entire composition range. From these measured values, the following thermodynamic and transport parameters which are useful for understanding the nature of the interaction of ethyl acetate with ethanol are evaluated. The Present Study has been divided into 3 parts:

- Study of variation in adiabatic compressibility, molar volume, mean free length, viscosity and related parameters at two temperatures 303.15 and 313.15 K
- Study of variation in free volume, internal pressure, enthalpy and gibbs free energy of activation and their excess parameters at two temperatures 303.15 and 313.15 K
- Estimating the variation of theoretical velocities using nomoto relation (nom) and Vandael Vangeel ideal mixing relation (Van) at two temperatures 303.15 and 313.15 K.

An attempt has been made to compare the merits of the relations for the binary liquid mixtures investigated at different temperatures. The results are explained in terms of intermolecular interactions occurring in these binary system. 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.

The data obtained can be used to understand intermolecular interactions between the unlike molecules and to test the theories of solutions. The departure of this real mixture from ideal behavior can be explained in terms of effect of hydrogen bond breaking, loss of dipolar association, differences in size and shapes, dipole-dipole interactions between different component molecules.

### Formulas:

$$\text{Density } \rho = \frac{\text{Weight of the liquid}}{\text{Weight of water}} \times \text{density of water at that temperature} \quad (1)$$

$$\text{Velocity} = \text{Average distance} \times 800 \text{ m/sec} \quad (2)$$

$$\text{Viscosity } n = \frac{\left(\rho_1 t_1 \times \eta_w\right) / \rho_w t_w}{\frac{\text{Density of liquid} \times \text{Time taken for liquid} \times \text{Viscosity of water}}{\text{Density of water} \times \text{Time taken for water}}} \quad (3)$$

$$\text{Number of moles of common compound } N_1 = \frac{\rho_1 V_1}{M_1} \quad (4)$$

$$\text{Number of moles of sub compound } N_2 = \frac{\rho_2 V_2}{M_2} \quad (5)$$

$$\text{The mole fraction of the first liquid } X_1 = \frac{N_1}{N_1 + N_2} \quad (6)$$

$$\text{Mole fraction of the second liquid } X_2 = \frac{N_2}{N_1 + N_2} \quad (7)$$

$$\text{Mean molecular weight: } M = M_1 X_1 + M_2 X_2 \quad (8)$$

$$\begin{aligned} \text{Molar volumes of the liquids } V_1 \text{ and } V_2: \\ V_1 = \frac{M_1}{\rho_1}; V_2 = \frac{M_2}{\rho_2} \end{aligned} \quad (9)$$

$$\text{Mean molar volume } V = \frac{M}{\rho} \quad (10)$$

$$\text{Excess volume } V^E = V - (V_1 X_1 + V_2 X_2) \quad (11)$$

Where:

$V$  = Experimental molar volume of the liquid mixture

$V_1$  = Mean molar volume of common compound

$V_2$  = Mean molar volume of sub compound

$X_1$  = Mole fraction of common compound

$X_2$  = Mole fraction of sub compound

$$\text{Adiabatic compressibility } \beta_{ad} = \frac{1}{\rho U_2} \quad (12)$$

Where:

$\rho$  = Density of the liquid mixture

$U$  = Velocity of the liquid mixture

$$\text{Deviation in adiabatic compressibility } \Delta \beta_{ad} = \beta_{ad} - (\beta_{ad1} X_1 + \beta_{ad2} X_2) \quad (13)$$

Where:

$\beta_{ad}$  = Adiabatic compressibility of the liquid mixture

$\beta_{ad1}$  = Adiabatic compressibility of the common compound

$\beta_{ad2}$  = Adiabatic compressibility of the sub compound

$X_1, X_2$  = The mole fractions of common and sub compounds, respectively

$$\text{Molar sound velocity (or) Rao's constant: } R = \frac{\bar{M}}{\rho^{1/3}} \quad (14)$$

$$\text{Wada's constant: } W = \frac{\bar{M}}{\rho} \times \frac{1}{\beta^{1/7}} \quad (15)$$

$$\text{Inter molecular free length: } L_f = K (\beta_{ad})^{1/2} \quad (16)$$

$K$  = Jacobson's constant

The values of  $K$  at the temperatures 30, 35, 40 and 45°C are:

- Temperature 30°, 35°, 40°, 45°
- Value of 'K' 627, 631.5, 636, 640.5

$$\text{Excess intermolecular free length: } L_f^E = L_{f \text{mix}} - (L_{f1} X_1 + L_{f2} X_2) \quad (17)$$

Where:

$L_{f \text{mix}}$  = Experimental inter molecular free length of the liquid mixture

$L_{f1}$  = Inter molecular free length of the common compound

$L_{f2}$  = Inter molecular free length of the sub compound

$$\text{Deviation in viscosity: } \Delta \eta = \eta_{\text{mix}} - (\eta_1 X_1 + \eta_2 X_2) \quad (18)$$

Where:

$\eta_{\text{mix}}$  = Experimental viscosity of the liquid mixture

$\eta_1$  = Viscosity of the common compound

$\eta_2$  = Viscosity of the sub compound

$$\text{Internal pressure: } \pi = \frac{bRT (Kh)^{1/2}}{U} \cdot \rho^{2/3} \cdot M^{7/6} \quad (19)$$

Where:

$b = 2$

$R = 8.3143$

$$\text{Excess internal pressure: } \pi^E = \pi_{\text{real}} - \pi_{\text{ideal}} \quad (20)$$

$$\text{Free volume: } V_f = (MV/K\eta)^{3/2} \quad (21)$$

$$\text{Excess free volume: } V_f^E = V_{f \text{real}} - V_{f \text{ideal}} \quad (22)$$

$$\text{Enthalpy: } H = \pi \cdot V_m \quad (23)$$

$$\text{Excess enthalpy: } H^E = H_{\text{real}} - H_{\text{ideal}} \quad (24)$$

$$\text{Excess Gibb's free energy: } G^E = RT \left[ \ln \eta V - (X_1 \ln \eta_1 V_1 + X_2 \ln \eta_2 V_2) \right] \quad (25)$$

$$R = 1.987$$

$$\text{Nomoto equation } U_{\text{Nomoto}} = \left[ (X_1 R_1 + X_2 R_2) / (X_1 V_1 + X_2 V_2) \right]^3 \quad (26)$$

$$\text{Van Dael and Vangeel equation: } 1 / (X_1 M_1 + X_2 + M_2)$$

$$*1/U_{\text{mix}}^2 = X_1 / M_1 U_1^2 + X_2 / M_2 U_2^2 \quad (27)$$

Where:

$U_{\text{mix}}$  = The ideal mixing ultrasonic velocity in liquid mixture

$U_1$  and  $U_2$  = Ultrasonic velocity in species

## RESULTS AND DISCUSSION

**Study of variation in adiabatic compressibility, molar volume, mean free length, viscosity and related paramters at two temperatures 303.15 and 313.15 K:** The experimentally measured values of ultrasonic velocity ( $U$ ) density ( $\rho$ ) and viscosity ( $\eta$ ) of the binary mixture and had been measured for the entire range of composition at two different temperatures 303.15 and 313.15 K. The molar volume ( $V_m$ ), adiabatic compressibility ( $\beta_{\text{ad}}$ ), intermolecular free length ( $L_f$ ), Rao's constant ( $R$ ) and Wada's constant ( $W$ ) were computed along with the measured values. The excess parameters such as excess molar Volume ( $V_m^E$ ), excess intermolecular free Length ( $L_f^E$ ) and deviations in adiabatic compressibility ( $\Delta\beta_{\text{ad}}$ ), deviations in viscosity ( $\Delta\eta$ ) and several other parameters have also been calculated and are presented in Table 1-3. The results are interpreted in terms of intermolecular interactions between the components of the mixtures.

Variation of ultrasonic velocity with composition of ethyl acetate is shown in Fig. 1, at different temperatures of measurement. The ultrasonic velocity non-linearly decreases with the mole fraction of ethyl acetate. The decrease in ultrasonic velocity in any solution indicates the maximum association among the molecules of the solution. The maximum association is due to the dipole-dipole interactions between the solute and solvent molecules. The effect of temperature is found to be considerable decrease in the values of ultrasonic velocity with increasing temperatures. Variation of Density with mole fraction of ethyl acetate + ethanol system is shown

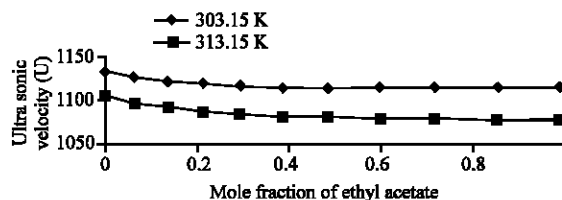


Fig. 1: Variation of ultrasonic velocity with molefraction of ethyl acetate+ethanol system

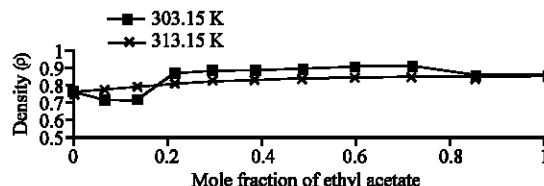


Fig. 2: Variation of density velocity with molefraction of ethyl acetate+ethanol system

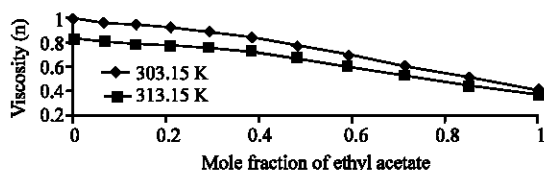


Fig. 3: Variation of viscosity velocity with molefraction of ethyl acetate+ethanol system

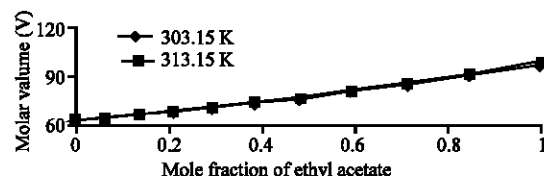


Fig. 4: Variation of molar volume with molefraction of ethyl acetate+ethanol system

in Fig. 2. The variation of viscosity with mole fraction of ethyl acetate is shown in Fig. 3 and deviation in viscosity in Fig. 4. From the fig, viscosity decreases regularly without having any maxima and decreases with increasing temperatures at any particular concentration of the liquid mixture. Same trend is observed at all the temperatures. It can be observed that deviations in viscosity ( $\Delta\eta$ ) are positive in the entire composition range at all the temperatures with a maximum at a mole fraction of 0.38 and the deviations in viscosity decrease with increase in temperature.

The molar Volumes ( $V$ ) and excess molar Volumes ( $V^E$ ) of this system are plotted in Fig. 3 and 4, respectively with the composition of ethyl acetate for the different

Table 1: Variation of  $U$ ,  $\rho$ ,  $\eta$ ,  $V_m$  at temperatures 303.15 and 313.15 K

Mole fraction X	Ultra sonic velocity (U) msec		$\rho \times (10^3 \text{ kg/m}^3)$		$\eta \text{ Cp}$		$V_m \text{ cm}^3 \text{ mol}^{-1}$	
	303.15 K	313.15 K	303.15 K	313.15 K	303.15 K	313.15 K	303.15 K	313.15 K
0.0000	1133.00	1104.00	0.7818	0.7748	0.9948	0.8299	61.3968	61.9515
0.0644	1128.80	1097.18	0.7348	0.7946	0.9923	0.8102	68.8377	63.6626
0.1340	1140.40	1091.78	0.7437	0.8128	1.0742	0.7930	71.7718	65.6787
0.2097	1119.80	1087.80	0.8870	0.8295	1.0415	0.7752	63.5983	68.0160
0.2922	1118.60	1084.03	0.9145	0.8452	0.9668	0.7550	65.3029	70.6657
0.3824	1118.20	1081.42	0.9175	0.8577	0.8664	0.7261	69.0337	73.8647
0.4815	1117.20	1080.73	0.9232	0.8639	0.8528	0.6686	72.9144	77.9372
0.5910	1117.00	1079.76	0.9322	0.8677	0.8133	0.5996	76.9187	82.6465
0.7124	1116.90	1078.63	0.9384	0.8711	0.7705	0.5247	81.6000	87.9176
0.8479	1116.20	1077.54	0.8886	0.8739	0.4037	0.4458	92.2885	93.8507
1.0000	1115.90	1076.00	0.8886	0.8758	0.4038	0.3652	99.1560	100.6052

Table 2: Variation of  $\beta_{ad}$ ,  $L_f$ ,  $R$ ,  $W$  at temperatures 303.15 and 313.15 K

Mole fraction X	$\beta_{ad} 10^{12} \text{ m}^2 \text{ N}^{-2}$		$L_f 10^{10} \text{ m}$		$R$		$W$	
	303.15 K	313.15 K	303.15 K	313.15 K	303.15 K	313.15 K	303.15 K	313.15 K
0.0000	99.64250	105.89400	0.6259	0.6545	2971	2972	1648	1648
0.0644	106.80630	104.54550	0.6480	0.6503	3327	3048	1829	1697
0.1340	103.39220	103.21820	0.6375	0.6462	3480	3139	1916	1754
0.2097	89.90740	101.87740	0.5945	0.6419	3065	3247	1732	1820
0.2922	87.39100	100.67730	0.5861	0.6382	3146	3369	1786	1894
0.3824	87.16760	99.70080	0.5854	0.6350	3326	3519	1889	1982
0.4815	86.78450	99.10970	0.5841	0.6332	3512	3712	1996	2093
0.5910	85.97740	98.84390	0.5814	0.6323	3704	3936	2109	2221
0.7124	85.42470	98.67120	0.5795	0.6318	3930	4185	2239	2363
0.8479	90.32540	98.55660	0.5959	0.6314	4444	4466	2512	2523
1.0000	90.37390	98.62130	0.5961	0.6316	4774	4785	2699	2704

Table 3: Variation of  $V_m^E$ ,  $\Delta\beta_{ad}$ ,  $\Delta\eta_{cp}$ ,  $L_f^E$  temperatures 303.15 and 313.15 K

Mole fraction X	$V_m^E \text{ cm}^3 \text{ mol}^{-1}$		$\Delta\beta_{ad} 10^{10} \text{ m}^2 \text{ N}^{-1}$		$\Delta\eta_{cp}$		$L_f^E 10^{-10} \text{ m}$	
	303.15 K	313.15 K	303.15 K	313.15 K	303.15 K	313.15 K	303.15 K	313.15 K
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0644	-0.5500	-0.7800	-0.6600	-0.8800	0.0148	0.0102	-0.0021	-0.0027
0.1340	-1.1420	-1.4600	-1.4000	-1.7000	0.0330	0.0255	-0.0044	-0.0053
0.2097	-1.7320	-2.0500	-2.1576	-2.4900	0.0532	0.0429	-0.0068	-0.0078
0.2922	-2.2840	-2.5900	-2.7800	-3.0900	0.0720	0.0610	-0.0088	-0.0097
0.3824	-2.6320	-2.8800	-3.0800	-3.4100	0.0830	0.0740	-0.0098	-0.0107
0.4815	-2.3520	-2.6400	-2.9400	-3.2800	0.0710	0.0626	-0.0094	-0.0103
0.5910	-1.8190	-2.1600	-2.4500	-2.7500	0.0535	0.0445	-0.0078	-0.0086
0.7124	-1.1900	-1.5800	-1.7500	-2.0400	0.0342	0.0260	-0.0056	-0.0064
0.8479	-0.5610	-0.8800	-0.9089	-1.1700	0.0150	0.0100	-0.0029	-0.0037
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

temperatures of observation. Here, also the excess volumes remain entirely negative reaching a minimum at about 0.38 mole fraction of ethyl acetate. It is also clear that there is an increasing trend of the excess molar volume curves with increasing temperature.

The non-linear variation of adiabatic compressibility observed from Fig. 5-9 represents the variation of deviation in adiabatic compressibility with mole fraction of ethyl acetate. The negative deviation of adiabatic compressibility reaches a maximum at about 0.38 mole fraction of ethyl acetate.

Variation of intermolecular free Length ( $L_f$ ) and excess intermolecular free Length ( $L_f^E$ ) is plotted with the composition of ethyl acetate in the mixture is shown in Fig. 9-12.

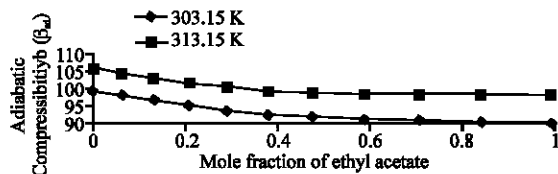


Fig. 5: Variation of adiabatic compressibility with molefraction of ethyl acetate+ethanol system

Figure 7 and 8 show the variation of Rao's Constant and Wada's Constant exhibit marked deviation from linearity with increasing the concentration of ethyl acetate. The extent of departure from linearity can be taken as a measure of interaction between unlike molecules.

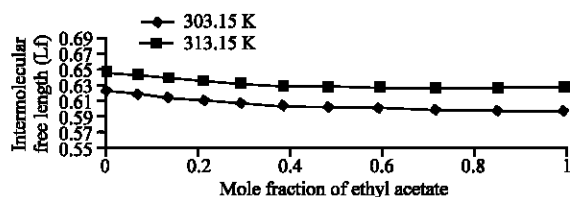


Fig. 6: Variation of intermolecular free length with molefraction of ethyl acetate+ethanol system

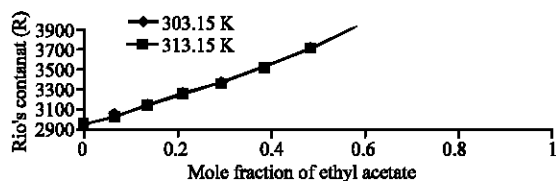


Fig. 7: Variation of Rao's constant with molefraction of ethyl acetate+ethanol system

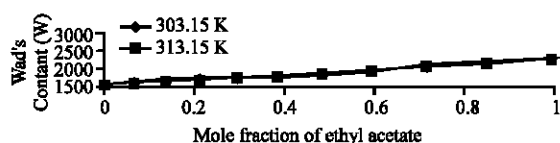


Fig. 8: Variation of Wada's constant with molefraction of ethyl acetate+ethanol system

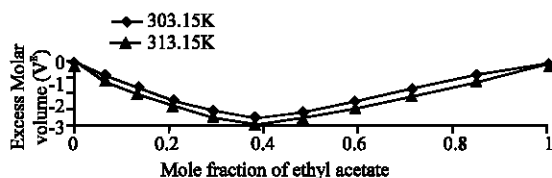


Fig. 9: Variation of excess molar volume with molefraction of ethyl acetate+ethanol system

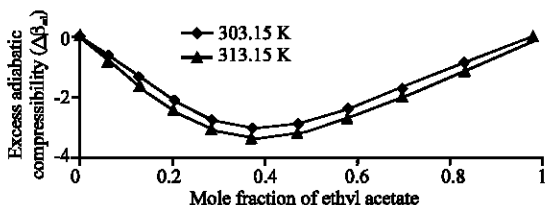


Fig. 10: Variation of deviation in adiabatic compressibility with molefraction of ethyl acetate for ethyl acetate+ethanol system

These results are favoring the dipole-dipole interactions between unlike molecules in binary mixtures. The excess values ( $V^E$ ,  $L_f^E$ ,  $\Delta\beta_{ad}$  and  $\Delta\eta$ ) are fitted in to an empirical equation of the form:

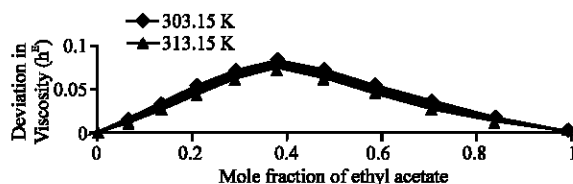


Fig. 11: Variation of deviation in viscosity with molefraction of ethyl acetate ethanol for acetate+ethanol system

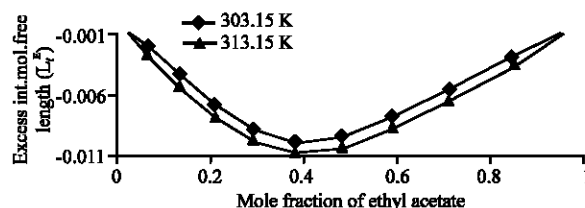


Fig. 12: Variation of excess inter molecular free length with molefraction of ethyl acetate ethanol for acetate+ethanol system

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

Where:

$A^E$  = The excess parameter

$X_1$  and  $X_2$  = The mole fraction of the two components

The coefficients A, B and C evaluated form linear least square method are given in Table. The standard deviations  $\sigma$  of ( $A^E$ ) are evaluated by the following relation:

$$s(A^E) = S(A_{exp}^E - A_{eq}^E) / (m-n)^{1/2}$$

Where:

$m$  = Number of experimental data and

$n$  = The number of coefficients

The results of the excess values indicate that the agreement between the experimental and theoretical values of the excess values is in satisfactory (Table 4-7).

**Study of variation in free volume, internal pressure, enthalpy and gibbs free energy of activation and their excess parameters at two temperatures 303.15 and 313.15 K:** In order to substantiate the presence of interaction between the molecules, it is essential to study the excess parameters like free volume, internal pressure and enthalpy. The deviation of physical property of the liquid mixtures from the ideal behavior is a measure of the interaction between the molecules which is attributed to either adhesive or cohesive forces.

Table 4: Variation molar volumes at 303.15 and 313.15 K

Mole fraction X	$(V_m^E)$	$(V_m^E)_{cal}$	$V_m^E$	$(V_m^E)_{cal}$
0.0000	0.0000	0.0000	0.0000	0.0000
0.0644	-0.5500	-0.5500	-0.7800	-0.7800
0.1340	-1.1420	-1.1620	-1.4600	-1.4860
0.2097	-1.7320	-1.7530	-2.0500	-2.1200
0.2922	-2.2840	-2.2940	-2.5900	-2.5980
0.3824	-2.6320	-2.6320	-2.8800	-2.8800
0.4815	-2.3520	-2.3620	-2.6400	-2.6520
0.5910	-1.8190	-1.1900	-2.1600	-2.2140
0.7124	-1.1900	-1.1850	-1.1850	-1.5750
0.8479	-0.5610	-0.5610	-0.8800	-0.8800
1.0000	0.0000	0.0000	0.0000	0.0000

Temperature 303.15 K, A = 0.0115, B = 1.8627, C = -3.1053,  $\sigma$  = 0.1797Temperature 313.15 K, A = -0.3019, B = 2.1804, C = -3.1501,  $\sigma$  = 0.1014Table 5: Deviation in adiabatic compressibility, A, B, C and  $\sigma$  values

Mole fraction X	$\Delta\beta_{ad}$	$(\Delta\beta_{ad})_{cal}$	$\Delta\beta_{ad}$	$(\Delta\beta_{ad})_{cal}$
0.0000	0.0000	0.0000	0.0000	0.0000
0.0644	-0.6600	-0.6600	-0.8800	-0.8800
0.1340	-1.4000	-1.4850	-1.7000	-1.7150
0.2097	-2.1576	-2.1426	-2.4900	-2.4890
0.2922	-2.7800	-2.7910	-3.0900	-3.1060
0.3824	-3.0800	-3.0800	-3.4100	-3.4100
0.4815	-2.9400	-2.9380	-3.2800	-3.2740
0.5910	-2.4500	-2.4480	-2.7500	-2.7540
0.7124	-1.7500	-1.7470	-2.0400	-2.0580
0.8479	-0.9089	-0.9089	-1.1700	-1.1700
1.0000	0.0000	0.0000	0.0000	0.0000

Temperature 303.15 K, A = -0.0602, B = -4.4070, C = 2.6483  $\sigma$  = 0.3020Temperature 313.15 K, A = -0.2518, B = -2.2784, C = 3.2046,  $\sigma$  = 0.9238

Table 6: Deviation in viscosity at 303.15 and 313.15 K

Mole fraction X	$\Delta\eta$	$(\Delta\eta)_{cal}$	$\Delta\eta$	$(\Delta\eta)_{cal}$
0.0000	0.0000	0.0000	0.0000	0.0000
0.0644	0.0148	0.0148	0.0102	0.0102
0.1340	0.0330	0.0324	0.0255	0.0254
0.2097	0.0532	0.0528	0.0429	0.0429
0.2922	0.0720	0.0710	0.0610	0.0624
0.3824	0.0830	0.0830	0.0740	0.0740
0.4815	0.0710	0.0721	0.0626	0.0616
0.5910	0.0535	0.0542	0.0445	0.0433
0.7124	0.0342	0.0351	0.0260	0.0190
0.8479	0.0150	0.0150	0.0100	0.0100
1.0000	0.0000	0.0000	0.0000	0.0000

Temperature 303.15 K, A = -0.1602, B = -2.4070, C = 2.3248,  $\sigma$  = 0.1020Temperature 313.15 K, A = -0.0518, B = -1.2584, C = 1.2146,  $\sigma$  = 0.0238

Table 7: Excess intermolecular free length at 303.15 and 313.15 K

Mole fraction X	$L^E$	$(L^E)_{cal}$	$L^E$	$(L^E)_{cal}$
0.0000	0.0000	0.0000	0.0000	0.0000
0.0644	-0.0021	-0.0021	-0.0027	-0.0027
0.1340	-0.0044	-0.0045	-0.0053	-0.0052
0.2097	-0.0068	-0.0067	-0.0078	-0.0079
0.2922	-0.0088	-0.0086	-0.0097	-0.0098
0.3824	-0.0098	-0.0098	-0.0107	-0.0107
0.4815	-0.0094	-0.0095	-0.0103	-0.0104
0.5910	-0.0078	-0.0079	-0.0086	-0.0087
0.7124	-0.0056	-0.0057	-0.0064	-0.0065
0.8479	-0.0029	-0.0029	-0.0037	-0.0037
1.0000	0.0000	0.0000	0.0000	0.0000

Temperature 303.15 K, A = -0.0702, B = -2.1070, C = 2.2483,  $\sigma$  = 0.0020Temperature 313.15 K, A = -0.0518, B = -2.3704, C = 1.2035,  $\sigma$  = 0.0238

**Internal pressure:** ( $\pi$ ) is the resultant of the forces of attraction and repulsion between the molecules in a liquid. The repulsive forces become prominent showing relatively lower values of internal pressure. But the concentrations where only one of the components is in large ratio, the internal pressure values are relatively

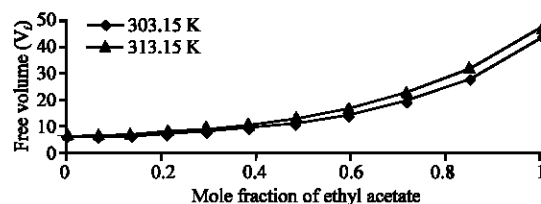


Fig. 13: Variation of free volume with molefraction of ethyl acetate+ethanol system

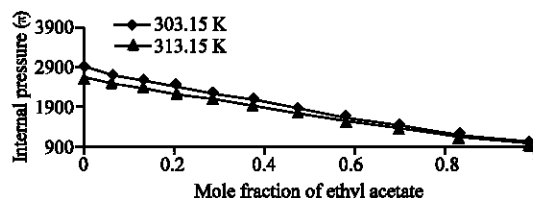


Fig. 14: Variation of internal pressure with molefraction of ethyl acetate+ethanol system

higher predicting greater forces of attraction between the molecules. Internal pressure maximum when the intermolecular association is strongest. Variation of Internal pressure in the binary system at two temperatures is shown Fig. 13.

**Free Volume ( $V_f$ ):** Hirschfelder found that free volume of a solute molecule at a particular temperature and pressure depends only on the internal pressure of the liquid in which it is immersed (Chen *et al.*, 2017). The weakening of molecular association leads to a larger free volume available for molecular motion and the reverse effect gives rise to smaller free volume. Figure 14 the variation of free volume in the binary system at two temperatures.

The ratio can be molalities instead of mole fractions. As internal pressure is known to be an inverse function of free volume, the trend of the plots of free volume confirms the same. It is suggested that the behavior of internal pressure at different temperatures and concentrations may follow a specific mathematical function. A plot between the values of  $\log \pi$  and  $\log (1/V_f)$  resulted in a family of parallel straight lines with slope  $x$ . The decrease in free volume and increase in internal pressure with increase in ethyl acetate in Ethyl Acetate+Ethanol binary liquid mixture at two temperatures suggests the close packing of the molecules inside the shield which may be brought about by the increasing magnitude of interactions.

When ethanol is added to ethyl acetate it results in considerable decrease in intermolecular spaces between the molecules as suggested by Jacobson (Saini *et al.*, 2017). This contributes to increase in free volume and

hence the decrease in the internal pressure and enthalpy giving raise to the negative  $V_f^E$  and positive  $\pi^E$  and  $H^E$  values as its dilution causes disruption of the aromatic C-H bond stretching.

**Enthalpy:** Figure 15 shows that decrease of ethaply with increase in mole fraction of ethyl acetate.

**Excess parameters:** Excess values of Internal Pressure and Enthalpy ( $\pi^E$  and  $H^E$ ) are shown in Fig. 16 shows that first the graph increase, attain maximum value at 0.5 and 0.6 mole fraction of ethyl acetate respectively, then decrease with further increase in its concentration which indicate the strong intermolecular interaction between component molecules. The negative values of  $V_f^E$  decrease with increase in the concentration of ethyl acetate attain minimum value at about 0.5 mole fraction of ethyl acetate; indicate the presence of strong molecular interaction. The negative deviation of magnitude in  $V_f^E$  and positive values of  $\pi^E$  and  $H^E$  indicate the presence of

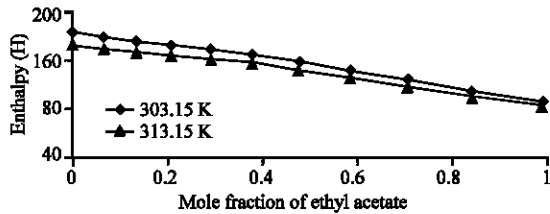


Fig. 15: Variation of enthalpy with molefraction of ethyl acetate+ethanol system

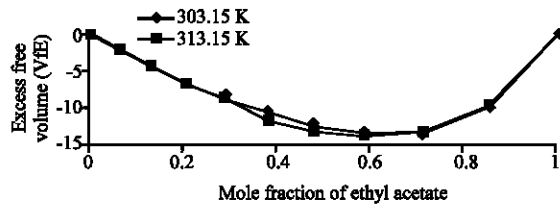


Fig. 16: Variation of excess free volume with molefraction of ethyl acetate+ethanol system

strong interaction between the hetero molecules of the mixture. Data presented in Table 8-13 as well as Fig.13-15 also indicate clearly that increase in temperature cause variation in the experimental values of all the excess thermodynamic properties as the local structure of the liquids are destroyed, thus, affecting their intermolecular free length and kinetic energy. Similar results were also observed earlier of several workers (Rao *et al.*, 2017). In the binary mixture of ethyl acetate+ethanol system, the excess values of  $\pi^E$  and  $H^E$  show positive, thus suggesting strong interaction between the mixing components of molecules. The variation of excess internal pressure ( $\pi^E$ ) is not positive. From the Table 8-13,  $H^E$  values are positive for ethyl acetate+ethanol, excess enthalpies being positive suggests that strong dipole-dipole interactions between the unlike molecules. 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 existing between ethyl acetate molecules is the main source of the energetic behavior. In general, the excess enthalpies are positive when the interactions between unlike molecules are stronger than the interaction between like molecules while positive enthalpies are shown when the interaction between like molecules are stronger (Kulkarni and Khadke, 2016; Artola *et al.*, 2017; Schmidt *et al.*, 2016). The experimental results of the excess enthalpies indicate that the dipole-dipole interaction between ethyl acetate and alcohols are stronger than the total interactions of ethyl acetate-ethyl acetate and alkonols.

**Excess free volume:** Figure 17 shows the variation of excess free volume in the binary system which is negative in the entire region.

**Excess Gibbs free energy:** Perusal of sign and magnitude of the parameters of Fig. 18, we find the strength of molecular interaction in the systems behave in the expected way. We also observe that  $G^E$  is positive for the binary system at the two temperatures. Positive  $G^E$  is

Table 8: Free volume, internal pressure and enthalpy at 303.15 and 313.15 K

Mole fraction X	Temperature 303.15 K			Temperature 313.15 K		
	$V_f \text{ Cm}^3 \text{ mol}^{-1}$	$\pi \text{ N/m}^2$	$H \text{ J/mole}$	$V_f \text{ Cm}^3 \text{ mol}^{-1}$	$\pi \text{ N/m}^2$	$H \text{ J/mole}$
0.0000	4.56510	2865.93	175.96	5.76250	2635.98	163.30
0.0644	5.08000	2710.56	171.52	6.40380	2499.07	159.10
0.1340	5.67450	2557.74	167.06	7.11530	2363.19	155.21
0.2097	6.38340	2404.01	162.47	7.95520	2224.45	151.30
0.2922	7.27690	2244.90	157.47	8.96950	2083.46	147.23
0.3824	8.52230	2070.00	151.53	10.3514	1928.51	142.45
0.4815	10.6391	1855.08	143.26	12.8224	1732.58	135.03
0.5910	13.8306	1634.58	133.86	16.5738	1529.52	126.41
0.7124	18.8266	1415.44	123.29	22.3069	1329.38	116.88
0.8479	27.2592	1199.00	111.33	31.5187	1134.22	106.45
1.0000	42.9102	986.54	97.82	47.2383	946.24	95.20



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

Mole fraction X	Temperature 303.15 K				Temperature 313.15 K			
	$V_f^E$ $\text{Cm}^3 \text{mol}^{-1}$	$\pi^E$ $\text{N/m}^2$	$H^E$ $\text{J/mole}$	$G^E$ $\text{Cal/mol}$	$V_f^E$ $\text{Cm}^3 \text{mol}^{-1}$	$\pi^E$ $\text{N/m}^2$	$H^E$ $\text{J/mole}$	$G^E$ $\text{Cal/mol}$
0.0000	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.0000
0.0644	-1.9534	-34.39	0.5871	20.31	-2.0317	-28.01	0.1862	15.4400
0.1340	-4.0307	-56.26	1.5768	42.72	-4.2131	-46.03	1.0501	36.1400
0.2097	-6.2233	-67.78	2.8986	66.74	-6.5143	-56.81	2.2942	59.6100
0.2922	-8.4920	-71.90	4.3410	90.29	-8.9225	-58.36	3.8448	84.1800
0.3824	-10.7063	-77.24	5.4540	109.74	-11.2844	-60.78	5.2118	106.2700
0.4815	-12.3907	-105.84	4.9309	115.08	-12.9256	-89.18	4.5471	109.0800
0.5910	-13.3952	-120.70	4.0771	111.30	-13.7123	-107.35	3.3756	100.7400
0.7124	-13.0547	-111.65	2.9981	95.29	-13.0129	-102.42	2.1067	81.5700
0.8479	-9.8170	-73.47	1.6191	60.85	-9.4161	-68.82	0.8979	49.1000
1.0000	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.0000	0.0000

Table 10: Excess free volumes at 303.15 and 313.15 K

Mole fraction X	$V_f^E$	$(V_f^E)_{\text{cal}}$	$V_f^E$	$(V_f^E)_{\text{cal}}$
0.0000	0.0000	0.0000	0.0000	0.0000
0.0644	-1.9534	-1.9534	-2.0317	-2.0317
0.1340	-4.0307	-4.1327	-4.2131	-4.2251
0.2097	-6.2233	-6.2453	-6.5143	-6.5121
0.2922	-8.4920	-8.4985	-8.9225	-8.9845
0.3824	-10.7063	-10.7063	-11.2844	-11.2844
0.4815	-12.3907	-12.3715	-12.9256	-12.9566
0.5910	-13.3952	-13.3352	-13.7123	-13.7343
0.7124	-13.0547	-13.1257	-13.0129	-13.1459
0.8479	-9.8170	-9.8170	-9.4161	-9.4161
1.0000	0.0000	0.0000	0.0000	0.0000

Temperature 303.15 K, A = -15.4993, B = -11.0431, C = -5.7744,  $\sigma$  = 0.2379, Temperature 313.15 K, A = -19.202, B = -12.715, C = -5.947,  $\sigma$  = 0.1027

Table 11: Excess internal pressures at 303.15 and 313.15 K

Mole fraction X	$\pi^E$	$(\pi^E)_{\text{cal}}$	$\pi^E$	$(\pi^E)_{\text{cal}}$
0.0000	0.00	0.00	0.00	0.00
0.0644	-34.39	-34.39	-28.01	-28.01
0.1340	-56.26	-56.13	-46.03	-46.11
0.2097	-67.78	-67.75	-56.81	-56.88
0.2922	-71.90	-71.92	-58.36	-58.37
0.3824	-77.24	-77.24	-60.78	-60.78
0.4815	-105.84	-105.74	-89.18	-89.19
0.5910	-120.70	-120.75	-107.35	-107.25
0.7124	-111.65	-111.71	-102.42	-102.38
0.8479	-73.47	-73.47	-68.82	-68.82
1.0000	0.00	0.00	0.00	0.00

Temperature 303.15 K, A = -10.6300, B = 56.6106, C = 14.6889,  $\sigma$  = 0.2356, Temperature 313.15 K, A = 4.46, B = 43.81, C = -37.44,  $\sigma$  = 1.80

Table 12: Excess enthalpy at 303.15 and 313.15 K

Mole fraction X	$H^E$	$(H^E)_{\text{cal}}$	$H^E$	$(H^E)_{\text{cal}}$
0.0000	0.0000	0.0000	0.0000	0.0000
0.0644	0.5871	0.5871	0.1862	0.1862
0.1340	1.5768	1.5734	1.0501	1.0501
0.2097	2.8986	2.8876	2.2942	2.2942
0.2922	4.3410	4.3580	3.8448	3.8448
0.3824	5.4540	5.4540	5.2118	5.2118
0.4815	4.9309	4.9289	4.5471	4.5471
0.5910	4.0771	4.0788	3.3756	3.3756
0.7124	2.9981	2.9975	2.1067	2.1067
0.8479	1.6191	1.6191	0.8979	0.8979
1.0000	0.0000	0.0000	0.0000	0.0000

Temperature 303.15 K, A = -15.4993, B = -11.0431, C = -5.7744,  $\sigma$  = 0.2379, Temperature 313.15 K, A = -19.202, B = -12.715, C = -5.947,  $\sigma$  = 0.1027

Table 13: Excess gibb's free energy at 303.15 and 313.15 K

Mole fraction X	$G^E$	$(G^E)_{\text{cal}}$	$G^E$	$(G^E)_{\text{cal}}$
0.0000	0.00	0.00	0.00	0.00
0.0644	20.31	20.31	15.44	15.44
0.1340	42.72	42.76	36.14	36.14
0.2097	66.74	66.82	59.61	59.61
0.2922	90.29	90.28	84.18	84.18
0.3824	109.74	109.74	106.27	106.27
0.4815	115.08	115.15	109.08	109.08
0.5910	111.30	111.29	100.74	100.74
0.7124	95.29	95.30	81.57	81.57
0.8479	60.85	60.85	49.10	49.10
1.0000	0.00	0.00	0.00	0.00

Temperature 303.15 K, A = -94.8446, B = 80.9613, C = 18.5457,  $\sigma$  = 2.9713, Temperature 313.15 K, A = -58.2253, B = 126.0754, C = -84.5877,  $\sigma$  = 1.3909

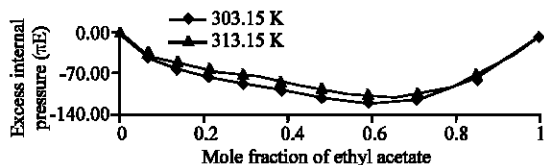


Fig. 17: Variation of excess internal pressure with mole fraction of ethyl acetate+ethanol

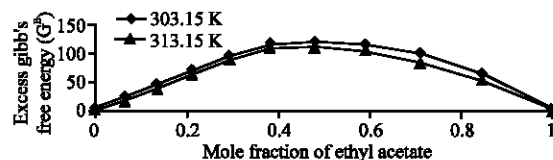


Fig. 18: Variation of excess Gibb's free energy with mole fraction of ethyl acetate for ethyl acetate+ethanol

indicative of strong molecular interaction (Sedov *et al.*, 2016; Gill *et al.*, 2016). Several attempts have been made by various workers (Ono *et al.*, 2016) relate  $G^E$  to chemical interaction. However,  $G^E$  and  $\eta^E$  are affected by different contributions where relative significance appears to vary with the chemical nature and the type of interacting molecules. Hence, a conclusion can be drawn that chemical forces are dominating over the physical forces in all the systems.

The excess energies of activation to the mixtures of ethyl acetate with alcohols are positive values. The  $\Delta G^E$  have local maxima at mole fraction about 0.5 for the system. The reason may be that the extent of interactions of alcohol molecules is a strong function of the composition in the mixtures, especially in the range dilute with respect to the associating component ethyl acetate. The values of  $\Delta G^E$  are found to be positive over the entire composition range. Like  $\Delta\rho$ , the negative  $\Delta G^E$  values are also indicative of the dominance of strong forces in these mixtures. Excess free volume, Excess internal pressure, Excess Enthalpy, and Excess Gibb's free energy of activation of viscous flow, excess molar volume, excess intermolecular free length, deviation in adiabatic compressibility and deviation in viscosity were calculated at different temperatures over the whole composition range and fitted to the Redlich-Kister equation to test the quality of the experimental values. Estimated coefficients and standard deviation values are also presented. The results of the excess values indicate that the agreement between the experimental and theoretical values of the excess values is satisfactory and are depicted in (Table 10-13). 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, 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 mixtures studied and the inherent nature of ethyl acetate predominant the existing strong interactions. From the ultrasonic velocity curves, the variation of ultrasonic velocity with the mole fraction of ethyl acetate at two different temperatures for the Ethyl Acetate+Ethanol system indicates that the ultrasonic velocity non-linearly varies with mole fraction and decreases with increasing temperatures at any particular concentration.

#### Estimating the variation of theoretical velocities using nomoto relation (nom) and vandael vangeel ideal mixing relation (van) at two temperatures 303.15 and 313.15 K:

Table 14: Nomoto relation (nom) and Vandael Vangeel ideal mixing relation (Van) at two temperatures 303.15 and 313.15 K

Mole fraction X	Temperature 303.15K						Temperature 313.15K					
	$U_{exp}$ m/sec	$U_{Nomoto}$	$U_{Vangeel}$	% $U_{No}$	% $U_{Vang}$	$U^2/U_{mix}^2$	$U_{exp}$ m/sec	$U_{Nomoto}$	$U_{Vangeel}$	% $U_{No}$	% $U_{Vang}$	$U^2/U_{mix}^2$
0.0000	1133.00	1133.00	1133.00	0.0000	0.0000	0.0000	1104.00	1104.00	1104.00	0.0000	0.0000	1.0000
0.0644	1127.61	1131.39	1119.62	0.3353	-0.7093	1.0143	1097.18	1101.20	1100.20	0.3665	-0.7093	1.0243
0.1340	1123.18	1129.68	1107.46	0.5792	-1.4000	1.0286	1091.78	1098.36	1095.36	0.6030	-1.2000	1.0386
0.2097	1119.80	1127.98	1096.75	0.7302	-2.0582	1.0425	1087.80	1095.53	1091.53	0.7103	-2.5582	1.0425
0.2922	1116.92	1126.27	1087.82	0.8373	-2.6051	1.0542	1084.03	1092.70	1089.70	0.7998	-2.8051	1.0522
0.3824	1114.68	1124.57	1081.09	0.8867	-3.0132	1.0631	1081.42	1089.89	1088.89	0.7829	-3.3315	1.0631
0.4815	1115.25	1122.86	1077.18	0.6824	-3.4140	1.0719	1080.73	1087.08	1085.08	0.5870	-3.7140	1.0719
0.5910	1115.91	1121.16	1076.95	0.4703	-3.4918	1.0737	1079.76	1084.28	1081.28	0.4180	-3.5180	1.0787
0.7124	1116.28	1119.46	1081.72	0.2850	-3.0960	1.0649	1078.63	1081.49	1078.49	0.2646	-3.5960	1.0649
0.8479	1116.20	1117.76	1093.56	0.1400	-2.0287	1.0418	1077.54	1078.70	1077.70	0.1086	-2.1029	1.0418
1.0000	1115.90	1115.90	1115.90	0.0000	1.0000	1.0000	1076.00	1076.00	1076.00	0.0000	0.0000	1.0000

The experimental values along with the values calculated theoretically using the relations of Nomoto and Van Dael ideal mixing for Ethyl acetate+Ethanol at the temperatures of 303.15 and 313.15 K are given in Table 14 and Fig. 19 and 20. It shows 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 (Padmanaban *et al.*, 2017). It is observed that the minimum percentage of deviation is exhibited by Nomoto relation and followed by Van Deal's relation. This is in good agreement with the conclusions drawn by others (Padmanaban *et al.*, 2017). Data reveal that the sound speed computed from Nomoto's Relation exhibits more satisfactory agreement with the experimental values in the temperatures range of 303.15 and 313.15 K. The ratio  $U^2_{exp}/U^2_{mix}$  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.

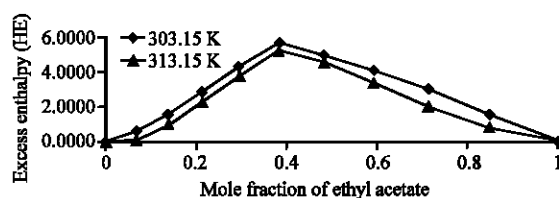


Fig. 19: Variation of excess enthalpy with mole fraction of ethyl acetate+ethanol

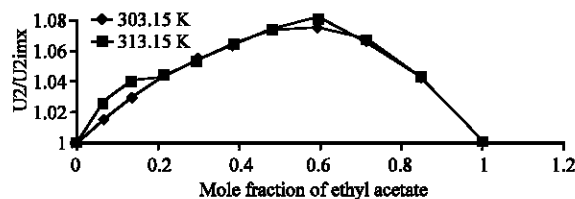


Fig. 20: Variation of  $U^2/U^2_{mix}$  with mole fraction of ethyl acetate+ethanol

## CONCLUSION

The results of these studies may be used for examining the suitability of these mixtures for practical applications such as in paints, varnishes, printing ink industries, bio-medical engineering, textile industry, leather industry and pharmaceutical industry. This study can be taken as a reference and the Thermodynamic properties of many other binary mixtures can be studied at different temperatures.

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