Estimating Various Thermodynamic and Excess Thermodynamic Properties of Binary Mixture of Ethyl Acetate with N-Propanol at 303.15k and 313.15k

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Abstract: Properties of liquid-liquid mixtures are thermodynamically very important as part of studies of thermodynamic, acoustic and transport aspects. 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. 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 n-Propanol 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 Propanol 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.

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

I. 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 [1-5]. 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. From a practical point of view, these properties are necessary for the development of thermodynamic models required in adequate and optimized process of the chemical, petrochemical, pharmaceutical and other industries .In addition, extensive information about structural phenomena of mixtures is of essential importance in the development of theories of the liquid state and predictive methods.

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

$$Y^E = Y^M{}_{real} - Y^M{}_{ideal}$$

Vander Waals and Van Laar [6] 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[7] and Scatchard [8-11] used Hildebrand's [12] concept of regular solutions to formulate a relation for excess volume.

Redlich and Kister [13] proposed an empirical equation to predict Y^E values for binary mixtures.

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

Where A_0, A_1 and A_2 are constants and X_1 and X_2 are the mole fractions of the two 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 or Rao's constant.

Jacobson [15] proposed an empirical relation between ultrasonic velocity, density and intermolecular free length. 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 303.15K and 313.15K. 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 +Propanol at the temperatures of 303.15K and 313.15K over the entire composition range have been studied. In addition, this study also provides a better insight into the nature of the molecular structure on volumetric properties and molecular interactions in the aforementioned binary system.

II. METHODOLOGY

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 $\pm$ 0.02 %. The densities of the liquid mixture (Ethyl Acetate + n-Propanol) 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 $\pm$ 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 $\pm$ 0.01K. 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 ($\square$). The excess volumes of mixing have been evaluated both as a formation 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 + n-Propanol, system has been chosen and studied its excess properties at the temperatures of 303.15K 313.15K 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 n-Propanol, are evaluated. The Present Study has been divided into 3 parts.

A. Study of Variation in Adiabatic Compressibility, Molar Volume, Mean Free Length, Viscosity and Related Parameters at Two Temperatures 303.15K and 313.15K

B. Study of Variation in Free Volume, Internal Pressure, Enthalpy And Gibbs Free Energy Of Activation And Their Excess Parameters At Two Temperatures 303.15K and 313.15K

C. Estimating The Variation Of Theoretical Velocities Using Nomoto Relation (Nom) & Vandael Vangeel Ideal Mixing Relation (Van) At Two Temperatures 303.15k And 313.15k

An attempt has been made to compare the merits of the relations for the binary liquid mixture investigated at different temperatures. The results are explained in terms of intermolecular interactions occurring in this binary system. The deviation in the variation of U^2_{exp} / U^2_{imx} 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.

III. RESULTS AND DISCUSSION

A. Study of Variation in Adiabatic Compressibility, Molar Volume, Mean Free Length, Viscosity and Related Paramters at Two Temperatures 303.15k And 313.15k

The experimentally measured values of ultrasonic velocity (U) density (ρ) and viscosity (η) of the binary mixture and had been measured for the entire range of composition at two different temperatures 303.15K and 313.15K. The molar volume (V_m), adiabatic compressibility (β_{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 ($\Delta\beta_{ad}$), deviations in viscosity ($\Delta\eta$) and several other parameters have also been calculated and are presented in Tables 1 to 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 1.1(a) at two different temperatures of measurement. Ultrasonic velocity (U) in this system is plotted with respect to mole fraction of ethyl acetate in Fig 1.1 for different temperatures. The curves of ultrasonic velocity indicate that the velocity decreases non-linearly with mole fraction of ethyl acetate and showed down ward trend indicating that there is a decrease in the velocity at a particular concentration of the mixture with an increase in temperature. Variation of Density with mole fraction of ethyl acetate + n-propanol system is shown in Fig 1.2. The composition dependence of viscosity (η) and deviation in viscosity ($\Delta\eta$) is shown in Fig 1.3 and Fig 3.3 for this mixture. The viscosity curves show positive deviations maximum at about 0.43 mole fraction of ethyl acetate. These results are favoring the dipole-dipole interactions between unlike molecules in binary mixtures.

The excess volumes (V^E) of mixing have been evaluated both as a formation of composition and temperature to examine the possibility of structural adjustment. The variation of molar volume (V) and excess molar volume (V^E) with mole fraction of ethyl acetate in this system is shown in Figs1.4 and 3.1 respectively. 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 0.43 mole fraction of ethyl acetate.

Variation of adiabatic compressibility (β_{ad}) and the deviation in adiabatic compressibility ($\Delta\beta_{ad}$) plotted against the mole fraction of ethyl acetate in the binary system for the different temperatures of study are shown in Fig 2.1 and Fig 3.2 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 0.43 mole fraction of ethyl acetate. The effect of temperature on the compressibility curves is in agreement with the idea that interaction between unlike molecules predominantly raptures the hydrogen-bonded structures, which is the main cause of deviation in adiabatic compressibility.

The structural changes are also found to influence the variation of intermolecular free length. In fact, when the liquid mixture assumes a less compressible phase of decreased flow capacity as evidenced by $\Delta\beta_{ad}$ versus composition curves and $\Delta\eta$ versus composition curves, the intermolecular free length might also be affected by the same structural changes. 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 2.2 and Fig 3.4.These curves indicated that the intermolecular free length varies non-linearly with mole fraction and increases slightly with increase in temperature.

The molar sound velocity (R) and molar compressibility (W) are the two important parameters, which are widely used for the study of physico-chemical behavior of liquid and liquid mixtures. The parameters (R) and (W) are also called Rao's constant and Wada's Constant respectively. For many liquid mixtures, Rao's empirical relation has been extensively used and verified by number of workers [16, 17] Molar compressibility (W) is found to be useful in understanding molecular interactions and structures of pure liquids and their solutions. The variation of Rao's constant and Wada's Constant [18] with composition of ethyl acetate is given in Figs 2.3 and 2.4. From the Figs, there is a linearity of these constants at all the temperatures. Further, over the temperature range 303.15 to 313.15K, the variations of these constants are almost negligible at any particular mole fraction. 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

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

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

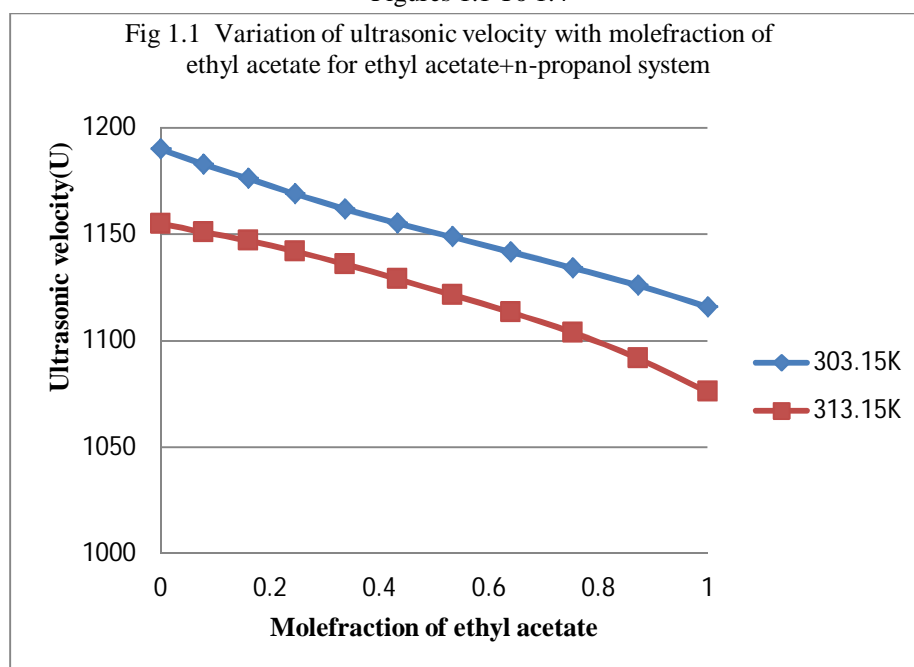$$\sigma (A^E) = \Sigma(A_{exp}^E - A_{eq}^E) / (m-n)^{1/2}$$

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

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

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		ρ x 10^{-3}kg/m^3		η Cp		V$_m$ cm^{-3}mol^{-1}	
	303.15K	313.15K	303.15K	313.15K	303.15K	313.15K	303.15K	313.15K
0.0000	1190.00	1155.00	0.7957	0.7863	1.7215	1.3685	75.5310	76.4339
0.0780	1182.91	1151.01	0.8123	0.7991	1.6387	1.3041	76.6745	77.4201
0.1600	1176.25	1147.04	0.8287	0.8106	1.5525	1.2412	77.9303	78.6806
0.2461	1168.92	1142.00	0.8446	0.8220	1.4622	1.1769	79.3154	80.1328
0.3368	1161.88	1136.02	0.8590	0.8330	1.3637	1.1082	80.9477	81.8146
0.4324	1155.15	1129.06	0.8711	0.8434	1.2468	1.0245	82.8960	83.7851
0.5333	1148.75	1121.44	0.8775	0.8498	1.1040	0.9118	85.5097	86.4040
0.6399	1141.75	1113.43	0.8809	0.8544	0.9444	0.7857	88.5698	89.5323
0.7529	1134.24	1103.86	0.8833	0.8597	0.7734	0.6514	91.9183	92.9625
0.8727	1126.03	1091.69	0.8854	0.8668	0.5926	0.5102	95.4886	96.6383
1.0000	1115.90	1076.00	0.8886	0.8758	0.4038	0.3652	99.1560	100.6052

Figures 1.1 To 1.4

Fig 1.1 Variation of ultrasonic velocity with molefraction of ethyl acetate for ethyl acetate+n-propanol system

Fig 1.2 Variation of Density with molefraction of ethyl acetate + Propanol system

Fig 1.3 Variation of viscosity with molefraction of ethyl acetate for ethyl acetate+n-propanol system

Fig 1.4 Variation of molar volume with molefraction of ethyl acetate for ethyl acetate+n-propanol system
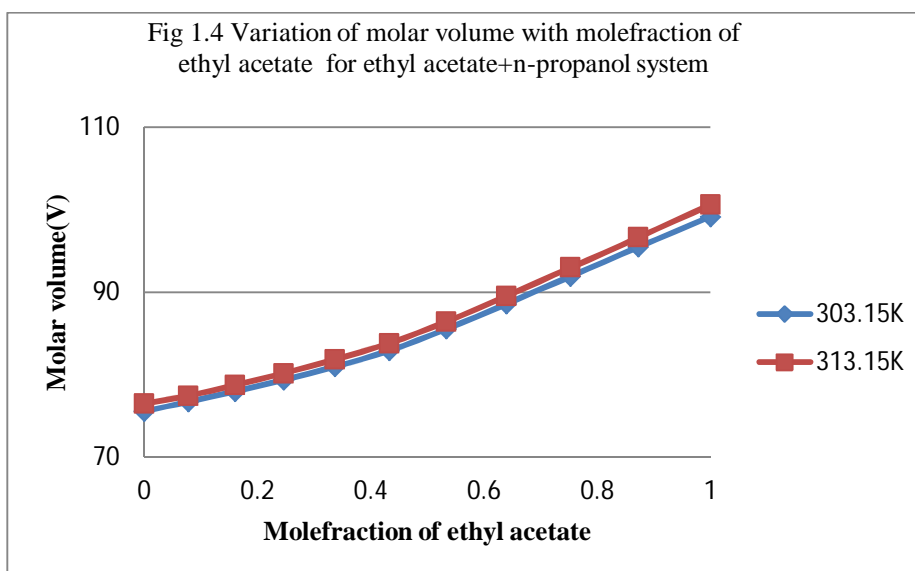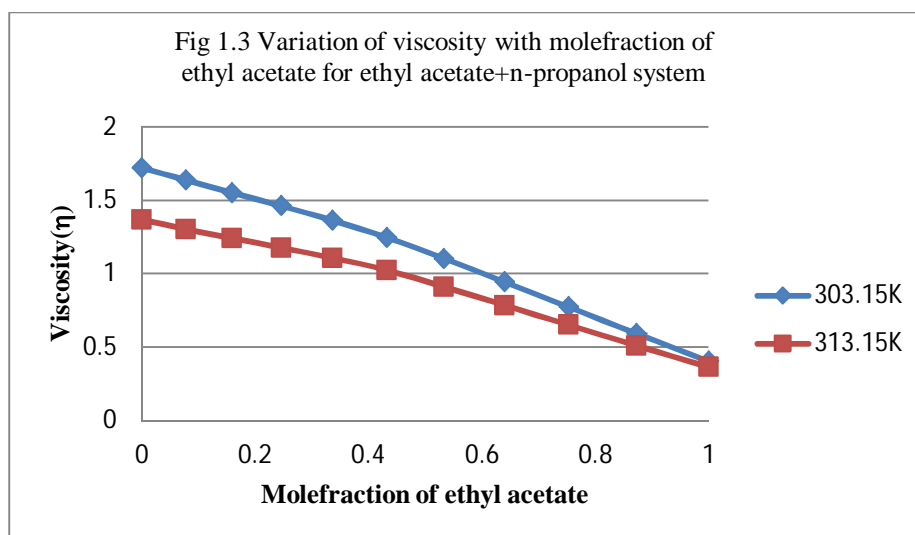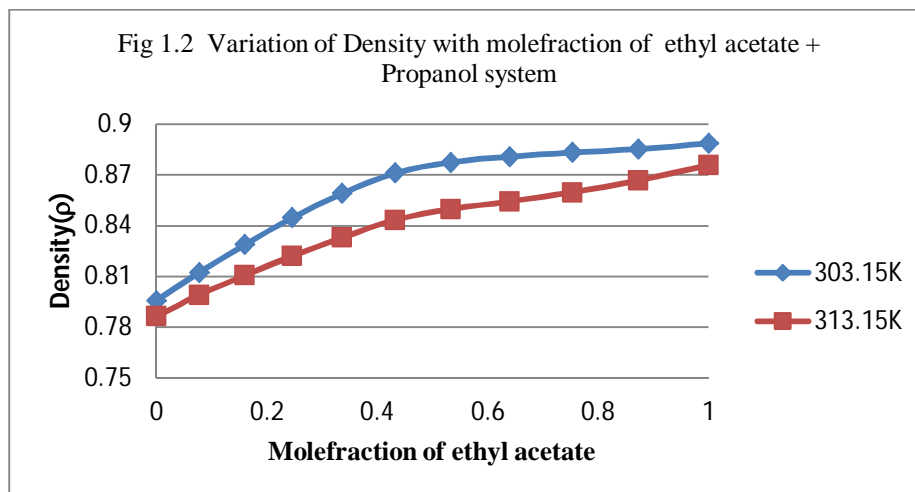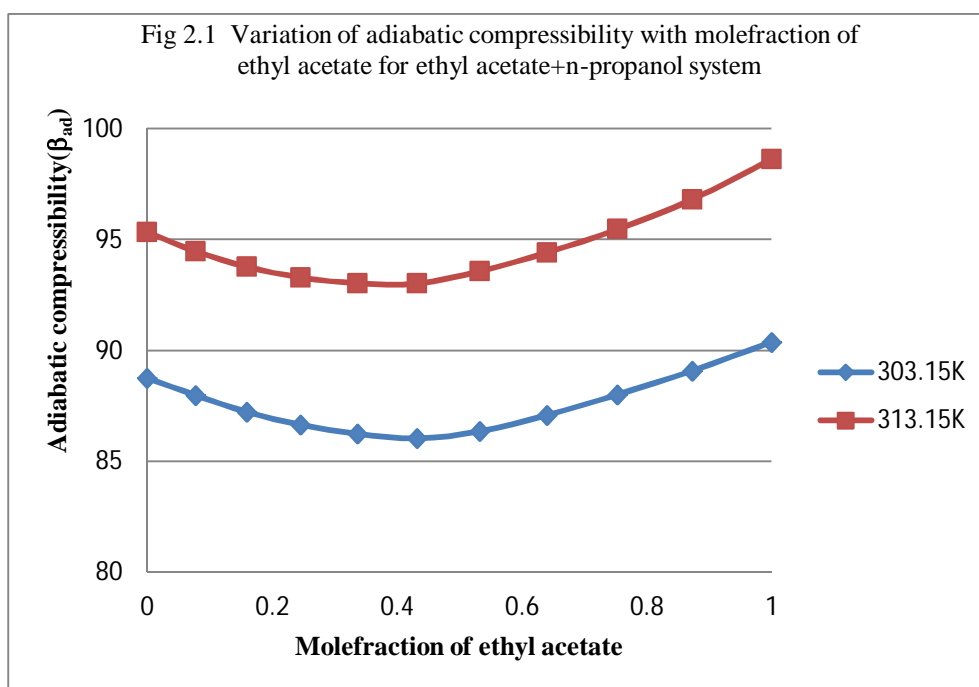
Table 2: Variation Of β_{Ad}, L_f, R, W At Temperatures 303.15k And 313.15k

Figures 2.1 To 2.4

Mole Fraction X	$\beta_{ad}\ 10^{12} m^2 N^{-2}$		$L_f\ 10^{-10}$ m		R		W	
	303.15K	313.15K	303.15K	313.15K	303.15K	313.15K	303.15K	313.15K
0.0000	88.7476	95.3340	0.5907	0.6210	3715	3722	2061	2065
0.0780	87.9745	94.4605	0.5881	0.6181	3764	3766	2095	2094
0.1600	87.2178	93.7599	0.5856	0.6158	3818	3823	2132	2130
0.2461	86.6479	93.2830	0.5836	0.6143	3878	3888	2172	2171
0.3368	86.2353	93.0211	0.5823	0.6134	3950	3962	2218	2218
0.4324	86.0308	93.0154	0.5816	0.6134	4037	4050	2272	2271
0.5333	86.3549	93.5670	0.5827	0.6152	4157	4167	2343	2340
0.6399	87.0784	94.4077	0.5851	0.6180	4297	4307	2423	2422
0.7529	88.0020	95.4590	0.5882	0.6214	4449	4459	2511	2511
0.8727	89.0769	96.8028	0.5918	0.6258	4611	4619	2604	2605
1.0000	90.3739	98.6213	0.5961	0.6316	4774	4785	2699	2704

Fig 2.1 Variation of adiabatic compressibility with molefraction of ethyl acetate for ethyl acetate+n-propanol system

Fig 2.2 Variation of intermolecular free length with molefraction of ethyl acetate for ethyl acetate+n-propanol system

Fig 2 .3 Variation of Rao's constant with molefraction of ethyl acetate for ethyl acetate+n-propanol system

Fig 2.4 Variation of Wada's constant with molefraction of ethyl acetate for ethyl acetate+n-propanol system
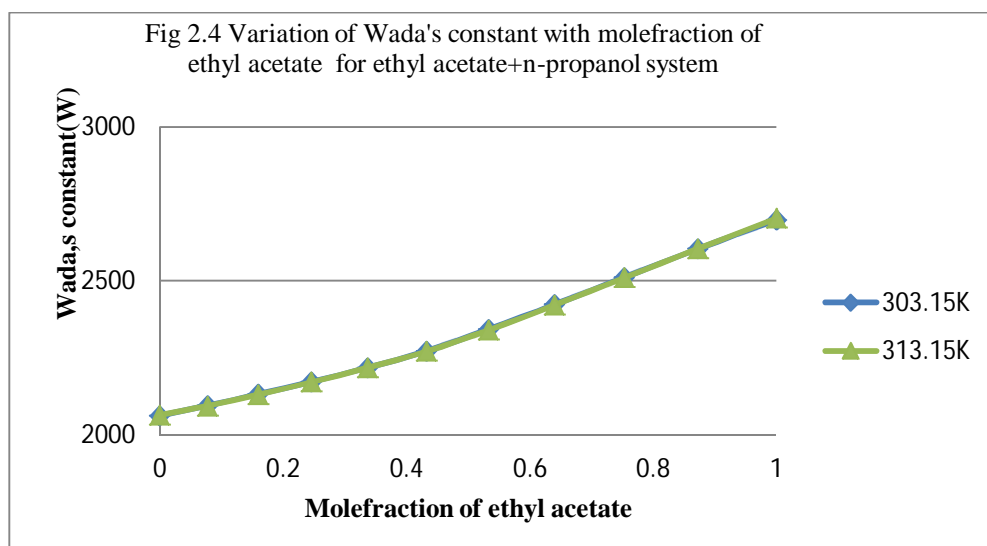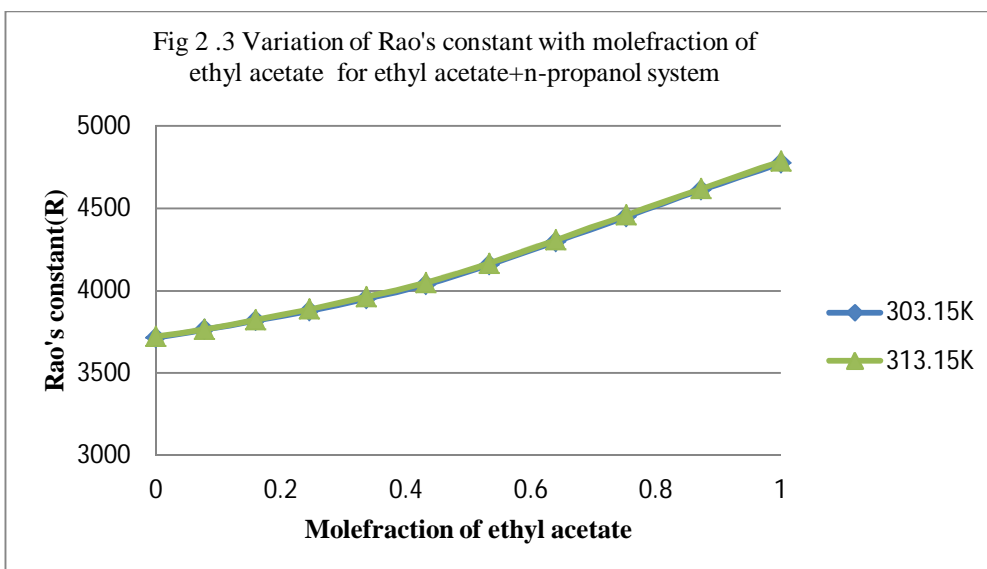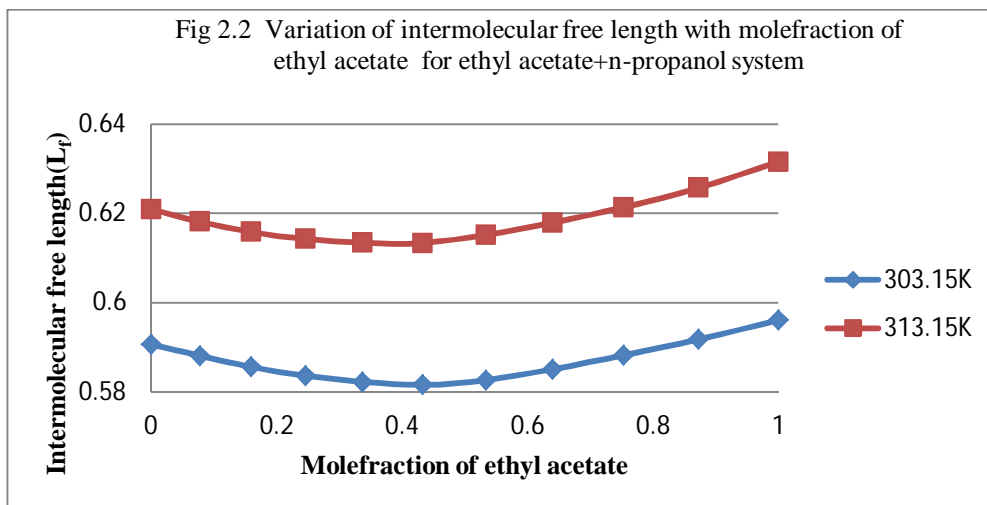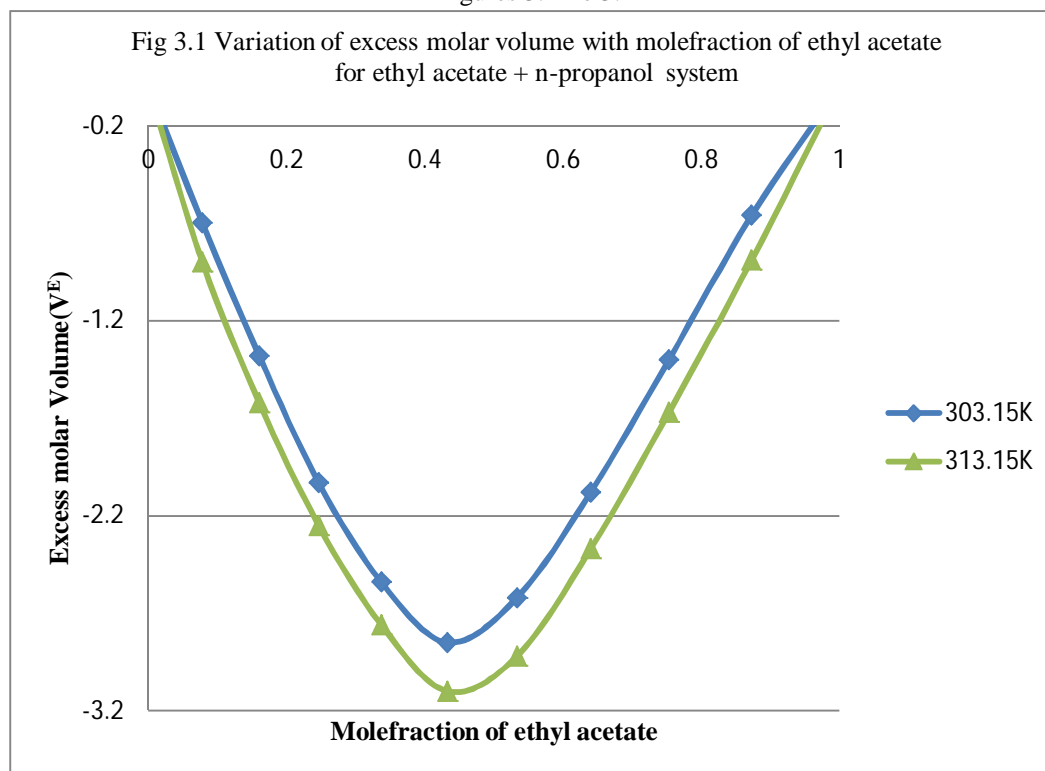
Table 3: Variation Of Vme , □□Ad , □□□Cp, L F E Temperatures 303.15k & 313.15k

Mole Fraction X	V_m^E Cm^3 mol^{-1}		β_{ad} 10^{10}m^2 N^{-1}		cp		L_f^E10^{-10}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
0.0780	-0.7000	-0.9000	-0.9000	-1.1300	0.0200	0.0139	-0.0030	-0.0037
0.1600	-1.3800	-1.6200	-1.7900	-2.1000	0.0418	0.0332	-0.0060	-0.0069
0.2461	-2.0300	-2.2500	-2.5000	-2.8600	0.0650	0.0553	-0.0084	-0.0093
0.3368	-2.5400	-2.7600	-3.0600	-3.4200	0.0860	0.0776	-0.0103	-0.0112
0.4324	-2.8500	-3.1000	-3.4200	-3.7400	0.0950	0.0898	-0.0115	-0.0122
0.5333	-2.6200	-2.9200	-3.2600	-3.5200	0.0852	0.0783	-0.0109	-0.0114
0.6399	-2.0800	-2.3700	-2.7100	-3.0300	0.0662	0.0593	-0.0091	-0.0098
0.7529	-1.4000	-1.6700	-1.9700	-2.3500	0.0440	0.0383	-0.0066	-0.0076
0.8727	-0.6600	-0.8900	-1.0900	-1.4000	0.0211	0.0173	-0.0036	-0.0045
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Figures 3.1 To 3.4

Fig 3.1 Variation of excess molar volume with molefraction of ethyl acetate for ethyl acetate + n-propanol system

Fig 3.2 Variation of deviation in adiabatic compressibility with molefraction of ethyl acetate for ethyl acetate + n-propanol system

Fig 3.3 Variation of deviation in viscosity with molefraction of ethyl acetate for ethyl acetate + n-propanol system

Fig 3.4 Variation of excess intermolecular free length with molefraction of ethyl acetate for ethyl acetate + n-propanol system

Table-4 Variation Of Molar Volumes At 303.15k And 313.15k

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Mole fraction X	TEMPERATURE 303.15K A = 0.8115 B = 1.2657 C = -2.1153 □□□□□□□□□□□□		TEMPERATURE 313.15K A = - 0.5529 B = 3.2514 C = - 1.1631 □□□□□□□□□□□□□□□□□□□□□□□□□□□□□□ □□□□□□□	
	(V_M^E)	$(V_m^E)_{cal}$	V_m^E	$(V_m^E)_{cal}$
0.0000	0.0000	0.0000	0.0000	0.0000
0.0780	-0.7000	-0.7000	-0.9000	-0.9000
0.1600	-1.3800	-1.3820	-1.6200	-1.6245
0.2461	-2.0300	-2.0350	-2.2500	-2.2521
0.3368	-2.5400	-2.5470	-2.7600	-2.7685
0.4324	-2.8500	-2.8500	-3.1000	-3.1000
0.5333	-2.6200	-2.6212	-2.9200	-2.9220
0.6399	-2.0800	-2.0842	-2.3700	-2.3770
0.7529	-1.4000	-1.4450	-1.6700	-1.6780
0.8727	-0.6600	-0.6600	-0.8900	-0.8900
1.0000	0.0000	0.0000	0.0000	0.0000

Table-5 Variation Of Deviation In Adiabatic Compressibility At 303.15k And 313.15k

Mole fraction X	TEMPERATURE 303.15K A = - 0.1502 B = -3.3370 C = 2.1253 □□□□□□□□□□□□□□□□□		TEMPERATURE 313.15K A = - 0.2518 B = - 2.2784 C = 1.2046 □□□□□□□□□□□□□□□□□□□□□□□□□□ □	
	□β_{ad}	$(□□\beta_{ad})_{cal}$	□β_{ad}	$(□□\beta_{ad})_{cal}$
0.0000	0.0000	0.0000	0.0000	0.0000
0.0780	-0.9000	-0.9000	-1.1300	-1.1300
0.1600	-1.7900	-1.7985	-2.1000	-2.1560
0.2461	-2.5000	-2.5105	-2.8600	-2.8650
0.3368	-3.0600	-3.0656	-3.4200	-3.4295
0.4324	-3.4200	-3.4200	-3.7400	-3.7400
0.5333	-3.2600	-3.2625	-3.5200	-3.5255
0.6399	-2.7100	-2.7175	-3.0300	-3.0325
0.7529	-1.9700	-1.9750	-2.3500	-2.3560
0.8727	-1.0900	-1.0900	-1.4000	-1.4000
1.0000	0.0000	0.0000	0.0000	0.0000

Table-6 Variation Of Deviation In Viscosityat At 303.15k And 313.15k

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Mole fraction X	TEMPERATURE 303.15K A = - 0.1802 B = 2.5215 C = -0.2523 □□□□□□□□□□□□□		TEMPERATURE 313.15K A = - 0.1531 B = 1.2584 C = -1.2146 □□□□□□□□□□□□□□□□□□□□□□□□□	
	□□	(□□□)$_{cal}$	□□	(□□□)$_{cal}$
0.0000	0.0000	0.0000	0.0000	0.0000
0.0780	0.0200	0.0200	0.0139	0.0139
0.1600	0.0418	0.0422	0.0332	0.0353
0.2461	0.0650	0.0645	0.0553	0.0562
0.3368	0.0860	0.0874	0.0776	0.0756
0.4324	0.0950	0.0950	0.0898	0.0898
0.5333	0.0852	0.0845	0.0783	0.0762
0.6399	0.0662	0.0658	0.0593	0.0574
0.7529	0.0440	0.0452	0.0383	0.0370
0.8727	0.0211	0.0211	0.0173	0.0173
1.0000	0.0000	0.0000	0.0000	0.0000

Table-7 Variation Of Excess Intermolecular Free Length At 303.15k And 313.15k

Mole fraction X	TEMPERATURE 303.15K A = - 0.0824 B = -1.1142 C = 2.2483 □□□□□□□□□□□□		TEMPERATURE 313.15K A = - 0.1256 B = - 2.0049 C = 1.2035 □□□□□□□□□□□□	
	L_f^E	(L_f^E)$_{cal}$	L_f^E	(L_f^E)$_{cal}$
0.0000	0.0000	0.0000	0.0000	0.0000
0.0780	-0.0030	-0.0030	-0.0037	-0.0037
0.1600	-0.0060	-0.0058	-0.0069	-0.0069
0.2461	-0.0084	-0.0092	-0.0093	-0.0093
0.3368	-0.0103	-0.0114	-0.0112	-0.0112
0.4324	-0.0115	-0.0115	-0.0122	-0.0122
0.5333	-0.0109	-0.0123	-0.0114	-0.0114
0.6399	-0.0091	-0.0091	-0.0098	-0.0098
0.7529	-0.0066	-0.0078	-0.0076	-0.0076
0.8727	-0.0036	-0.0036	-0.0045	-0.0045
1.0000	0.0000	0.0000	0.0000	0.0000

B. Study of Variation in Free Volume, Internal Pressure,Enthalpy and Gibbs Free Energy of Activation and their Excess Parameters at Two Temperatures 303.15k and 313.15k

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 [18].

1) Internal Pressure (π): 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 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 8.2.

2) Free Volume(V_f): Hirschfelder[19-20] 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. 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. Fig shows 8.1 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 + n-Propanol 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 n-Propanol is added to ethyl acetate it results in considerable decrease in intermolecular spaces between the molecules as suggested by Jacobson [21]. 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 π^E and H^E values as its dilution causes disruption of the aromatic C-H bond stretching.

3) Enthalpy: Fig 8.3 shows that decrease of Enthalpy with increase in Mole Fraction of Ethyl Acetate

4) Excess Parameters:

a) Excess values of Internal Pressure and Enthalpy (π^E & H^E) are shown in Figs 9.2 and 9.4 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 deviation of magnitude in V_f^E and positive values of π^E and H^E indicate the presence of strong interaction between the hetero molecules of the mixture. Data presented in Tables [from 8to 13] as well as Figs [8.1(b)&(c)] 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. In the binary mixture of ethyl acetate + Propanol 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. From the Tables8 to 13, H^E values are positive for ethyl acetate + n-Propanol, 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. The experimental results of the excess enthalpies indicate that the dipole-dipole interaction between ethyl acetate and alcohols are stronger.

b) Excess Free Volume: Fig 9.1 shows the Variation of excess free volume in the binary system which is negative in the entire region.
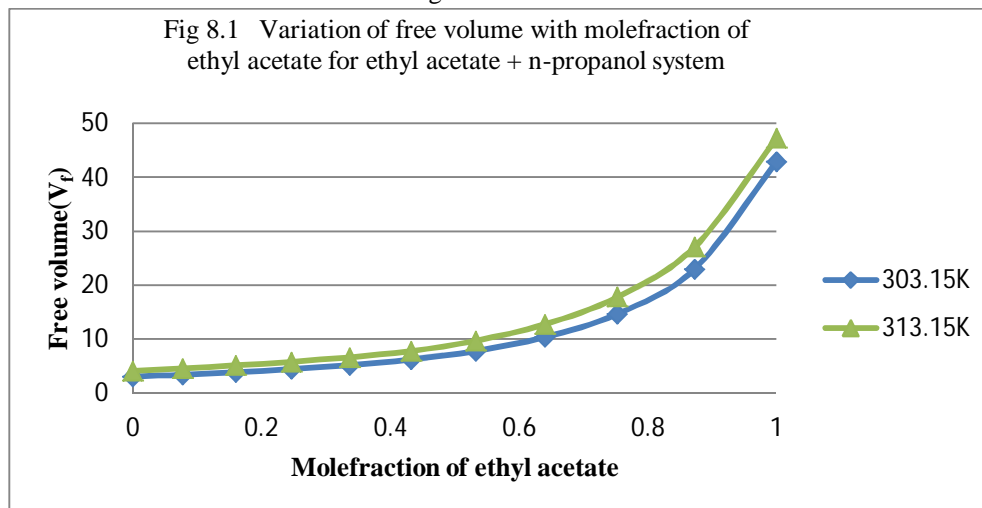
c) Excess Gibbs Free Energy: Perusal of sign and magnitude of the parameters of Fig 9.3 we find the strength of molecular interaction in the systems behave in the expected way. We also observe that G^E is positive for the binary system at the two temperatures. Positive G^E is indicative of strong molecular interaction [22, 23]. Several attempts have been made by various workers [24-28] relate G^E to chemical interaction. However, G^E and π^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 [29].

The excess energies of activation to the mixtures of ethyl acetate with alcohols are positive values. The ΔG^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 ΔG^E are found to be positive over the entire composition range. Like $\Delta\eta$, the negative ΔG^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 theatrical values of the excess values is satisfactory and are depicted in (Tables-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 + n-Propanol system indicates that the ultrasonic velocity non-linearly varies with mole fraction and decreases with increasing temperatures at any particular concentration.

Table -8 Variations Of Free Volume, Internal Pressure And Enthalpy At 303.15k And 313.15k

Mole Fraction X	Temperature 303.15K			Temperature 313.15K		
	V_f Cm^3mol^{-1}	$\square$ $\square\square m^2$	H J/mole	V_f Cm^3mol^{-1}	$\square$ $\square\square m^2$	H J/mole
0.0000	3.0242	2863.48	216.28	4.0799	2571.02	196.51
0.0780	3.4049	2725.07	208.94	4.5567	2456.94	190.22
0.1600	3.8653	2584.12	201.38	5.1107	2339.42	184.07
0.2461	4.4264	2441.13	193.62	5.7710	2219.33	177.84
0.3368	5.1498	2289.71	185.35	6.5949	2093.58	171.29
0.4324	6.1805	2120.72	175.80	7.7609	1951.78	163.53
0.5333	7.7918	1922.90	164.43	9.6932	1775.56	153.42
0.6399	10.3462	1708.95	151.36	12.7463	1582.70	141.70
0.7529	14.6734	1483.89	136.40	17.7998	1380.92	128.37
0.8727	22.9934	1245.50	118.93	27.0985	1169.77	113.04
1.0000	42.9102	986.54	97.82	47.2383	946.24	95.20

Figures 8.1 To 8.3

Fig 8.1   Variation of free volume with molefraction of ethyl acetate for ethyl acetate + n-propanol system

Fig 8.2 Variation of internal pressure with molefraction of ethyl acetate for ethyl acetate + n-propanol system

Fig 8.3 Variation of enthalphy with molefraction of ethyl acetate for ethyl acetate + n-propanol system
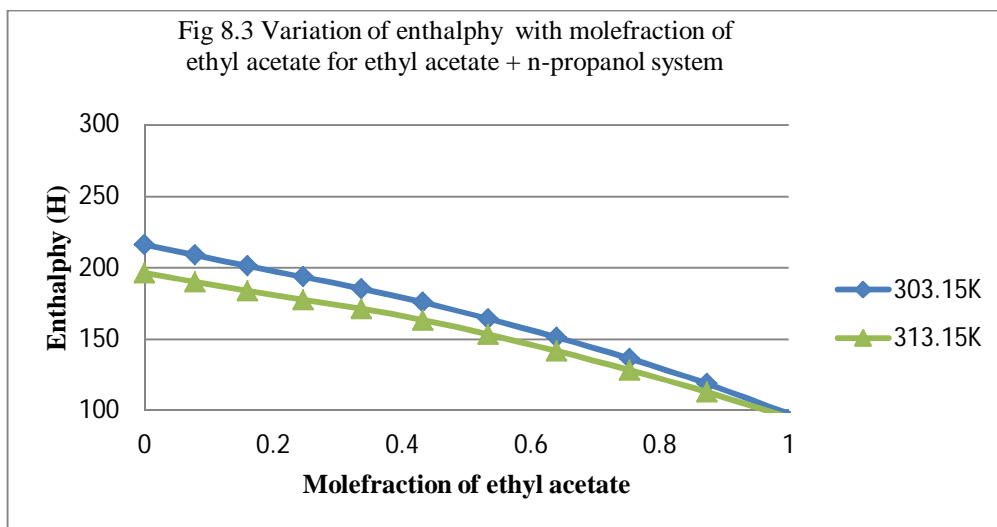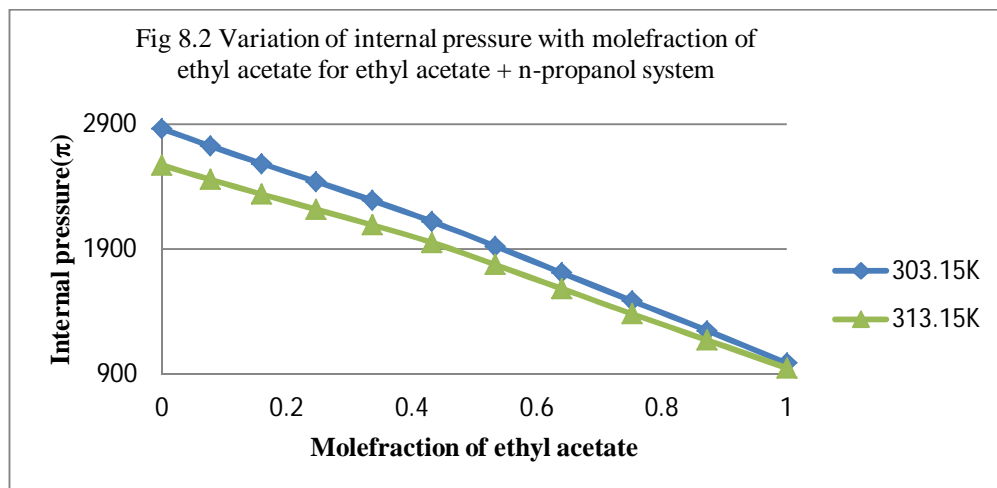
Table-9 Variation Of Excess Free Volume, Excess Internal Pressure Excess Enthalpyand Excess Gibb's Free Energy At 303.15k And 313.15k

Mole Fraction X	TEMPERATURE – 303.15K				TEMPERATURE 313.15K			
	V_f^E $Cm^3\,mol^{-1}$	π^E m^2	H^E J/mole	G^E Cal/mol	V_f^E $Cm^3\,mol^{-1}$	π^E m^2	H^E J/mole	G^E Cal/mol
0.0000	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.00	0.00
0.0780	-2.7317	8.05	1.9069	34.72	-2.8910	12.71	1.61	28.79
0.1600	-5.5395	20.90	4.0516	70.10	-5.8733	28.32	3.76	61.42
0.2461	-8.4143	39.59	6.4940	105.73	-8.9307	48.19	6.26	95.76
0.3368	-11.3078	58.37	8.9635	140.33	-12.0205	69.78	8.90	130.31
0.4324	-14.0896	68.79	10.7385	168.47	-14.9798	83.29	10.82	158.47
0.5333	-16.5028	60.36	11.3193	185.51	-17.4022	71.00	10.93	170.77
0.6399	-18.2030	46.62	10.8897	188.34	-18.9528	51.46	10.03	169.79
0.7529	-18.3810	33.56	9.3054	170.49	-18.7741	33.20	8.14	150.06
0.8727	-14.8395	20.03	6.0317	118.09	-14.6459	16.70	4.95	100.17
1.0000	0.0000	0.00	0.0000	0.00	0.0000	0.00	0.00	0.00

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Figures 9.1 To 9.4

Fig 9.1 Variation of excess free volume with molefraction of ethyl acetate for ethyl acetate + n-propanol system

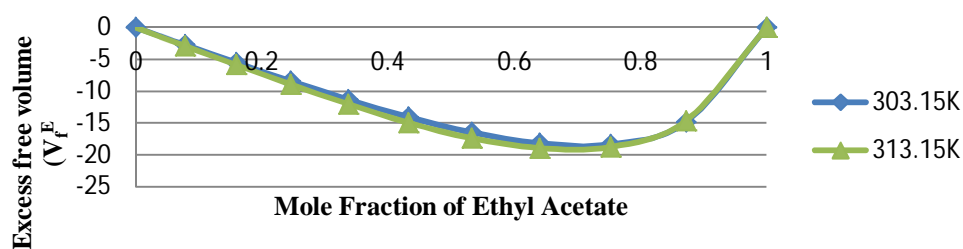Fig 9.2 Variation of excess internal pressure with molefraction of ethyl acetate for ethyl acetate + n-propanol system
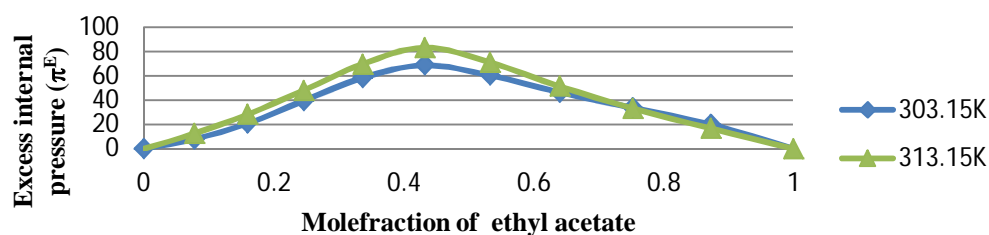

Fig 9.3 Variation of excess Gibb's free energy with molefraction of ethyl acetate for ethyl acetate + n-propanol system
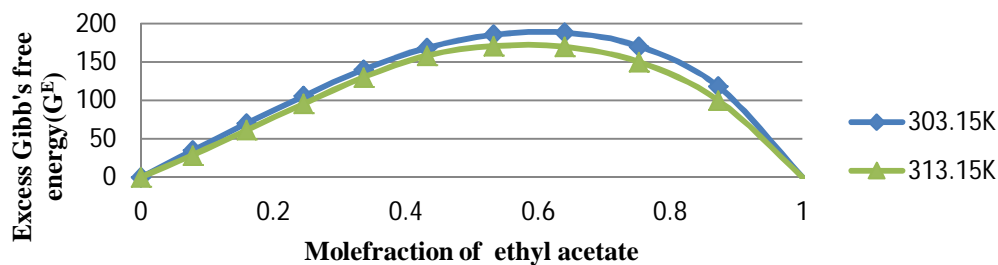

Fig 9.4 Variation of excess enthalpy with molefraction of ethyl acetate for ethyl acetate + n-propanol system
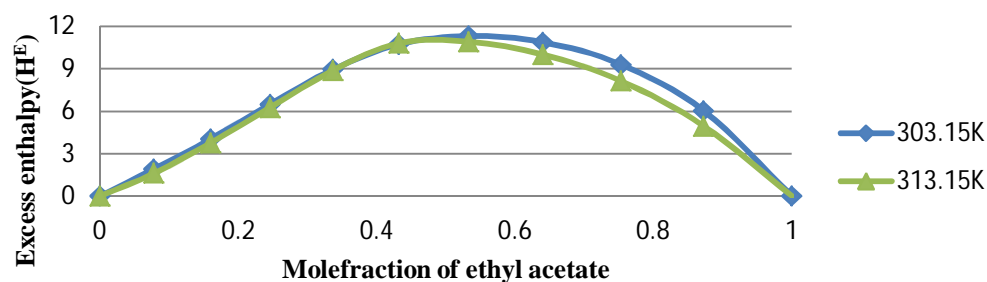
Table 10: Variation Of Excess Free Volumes At 303.15k And 313.15k

Mole fraction X	TEMPERATURE 303.15K A = -14.4592 B = -10.0441 C = -5.8754 ◻◻◻◻0.2478		TEMPERATURE 313.15K A = -18.222 B = -13.746 C = -6.955 ◻◻◻◻0.1226	
	V_f^E	$(V_f^E)_{cal}$	V_f^E	$(V_f^E)_{cal}$
0.0000	0.0000	0.0000	0.0000	0.0000
0.0780	-2.7317	-2.7317	-2.8910	-2.8910
0.1600	-5.5395	-5.5345	-5.8733	-5.8752
0.2461	-8.4143	-8.4253	-8.9307	-8.9345
0.3368	-11.3078	-11.3198	-12.0205	-12.0215
0.4324	-14.0896	-14.0896	-14.9798	-14.9798
0.5333	-16.5028	-16.5116	-17.4022	-17.4112
0.6399	-18.2030	-18.2213	-18.9528	-18.9652
0.7529	-18.3810	-18.3888	-18.7741	-18.7851
0.8727	-14.8395	-14.8395	-14.6459	-14.6459
1.0000	0.0000	0.0000	0.0000	0.0000

Table -11 Variation Of Excess Internal Pressures At 303.15k And 313.15k

Mole fraction X	TEMPERAUTURE 303.15K A = -11.6650 B = 54.6302 C = 15.6429 ◻◻◻◻◻0.3345		TEMPERAUTURE 313.15K A= 14.45 B= 43.812 C= -37.443 ◻◻◻◻◻◻◻◻◻	
	$\Box^E$	$(\Box^E)_{cal}$	$\Box^E$	$(\Box^E)_{cal}$
0.0000	0.00	0.00	0.00	0.00
0.0780	8.05	8.05	12.71	12.71
0.1600	20.90	20.95	28.32	28.38
0.2461	39.59	39.61	48.19	48.13
0.3368	58.37	58.44	69.78	69.79
0.4324	68.79	68.79	83.29	83.29
0.5333	60.36	60.42	71.00	71.12
0.6399	46.62	46.38	51.46	51.55
0.7529	33.56	33.45	33.20	33.22
0.8727	20.03	20.03	16.70	16.70
1.0000	0.00	0.00	0.00	0.00

Table-12 Variation Of Excess Enthalpy At 303.15k And 313.15k

Mole fraction X	TEMPERATURE 303.15K A = -16.4925 B = -10.0425 C = -6.7994 ⬚⬚⬚⬚0.3488		TEMPERATURE 313.15K A = -17.253 B = -13.752 C = -8.9551 ⬚⬚⬚⬚0.2563	
	H^E	$(H^E)_{cal}$	H^E	$(H^E)_{cal}$
0.0000	0.00	0.0000	0.00	0.00
0.0780	1.91	1.90	1.61	1.61
0.1600	4.05	4.06	3.76	3.74
0.2461	6.49	6.45	6.26	6.27
0.3368	8.96	8.97	8.90	8.93
0.4324	10.74	10.74	10.82	10.82
0.5333	11.32	11.4	10.93	10.95
0.6399	10.89	10.87	10.03	10.14
0.7529	9.31	9.33	8.14	8.15
0.8727	6.03	6.03	4.95	4.95
1.0000	0.00	0.0000	0.00	0.00

Table -13 Variation Of Excess Gibb's Free Energyat 303.15k And 313.15k

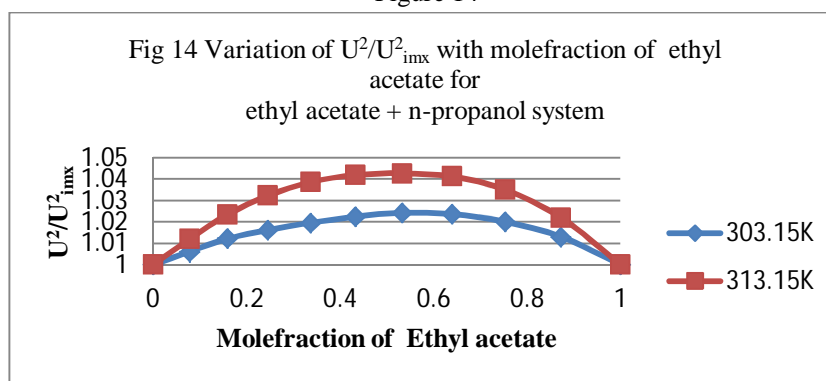| Mole fraction X	TEMPERATURE 303.15K A = - 95.5436 B = 81.9723 C = 18.5354 ⬚⬚⬚⬚2.3241		TEMPERATURE 313.15K A = -55.2023 B =121.0763 C = -85.5887 ⬚⬚⬚ 1.5369	
	G^E	$(G^E)_{cal}$	G^E	$(G^E)_{cal}$
0.0000	0.00	0.00	0.00	0.00
0.0780	34.72	34.72	28.79	28.79
0.1600	70.10	70.16	61.42	61.35
0.2461	105.73	105.85	95.76	95.79
0.3368	140.33	140.41	130.31	130.45
0.4324	168.47	168.47	158.47	158.47
0.5333	185.51	185.53	170.77	170.74
0.6399	188.34	188.38	169.79	169.72
0.7529	170.49	170.39	150.06	150.16
0.8727	118.09	118.09	100.17	100.17
1.0000	0.00	0.00	0.00	0.00

C. Estimating the Variation of Theoritical Velocities Using Nomoto Relation (Nom) & Vandael Vangeel Ideal Mixing Relation (Van) at Two Temperatures 303.15k and 313.15k

The experimental values along with the values calculated theoretically using the relations of Nomoto and Van Dael ideal mixing for Ethyl acetate + n-Propanol at the temperatures of 303.15 and 313.15K are given in Tables 14 and Fig 14. 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 [30] .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 [22]. 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 K and 313.15K. 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-14 Variation Of Nomoto Relation (Nom) & Vandael Vangeel Ideal Mixing Relation (Van) At Two Temperatures 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/U_{imx}^2	U_{exp} m/s	U_{Nomoto}	U_{idmx}	% U_{No}	% U_{imx}	U^2/U_{imx}^2
0.0000	1190.00	1190.00	1190.00	0.0000	0.0000	1.0000	1190.00	1190.00	1190.00	0.0000	0.0000	1.0000
0.0780	1182.91	1182.35	1179.30	-0.0476	-0.3054	1.0061	1182.91	1182.35	1179.30	-0.0476	-0.3054	1.0061
0.1600	1176.25	1174.86	1169.14	-0.1181	-0.6041	1.0122	1176.25	1174.86	1169.14	-0.1181	-0.6041	1.0122
0.2461	1168.92	1167.40	1159.57	-0.1296	-0.7992	1.0162	1168.92	1167.40	1159.57	-0.1296	-0.7992	1.0162
0.3368	1161.88	1159.97	1150.65	-0.1644	-0.9667	1.0196	1161.88	1159.97	1150.65	-0.1644	-0.9667	1.0196
0.4324	1155.15	1152.58	1142.44	-0.2228	-1.0999	1.0224	1155.15	1152.58	1142.44	-0.2228	-1.0999	1.0224
0.5333	1148.75	1145.21	1135.04	-0.3082	-1.1939	1.0243	1148.75	1145.21	1135.04	-0.3082	-1.1939	1.0243
0.6399	1141.75	1137.88	1128.53	-0.3391	-1.1576	1.0236	1141.75	1137.88	1128.53	-0.3391	-1.1576	1.0236
0.7529	1134.24	1130.58	1123.06	-0.3234	-0.9859	1.0200	1134.24	1130.58	1123.06	-0.3234	-0.9859	1.0200
0.8727	1126.03	1123.31	1118.78	-0.2421	-0.6438	1.0130	1126.03	1123.31	1118.78	-0.2421	-0.6438	1.0130
1.0000	1115.90	1115.90	1115.90	0.0000	0.0000	1.0000	1115.90	1115.90	1115.90	0.0000	0.0000	1.0000

Figure 14

Fig 14 Variation of U^2/U^2_{imx} with molefraction of ethyl acetate for ethyl acetate + n-propanol system

IV. CONCLUSIONS

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.

V.   CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this paper.

VI.   ACKNOWLEDGEMENTS

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SUPPLEMENTARY INFORMATION

A.   Formulae

1. Density $\rho = \dfrac{\text{Weight of the liquid}}{\text{Weight of water}} \times$ density of water at that temperature

2. Velocity = average distance x 800 m/s

3. Viscosity $\eta = (\rho_l t_l \times \eta_w)/\rho_w t_w = \dfrac{\text{density of liquid x Time Taken for liquid x Viscosity of water}}{\text{Density of water x Time Taken for water.}}$

4. Number of moles of common compound $N_1 = \dfrac{\rho_1 V_1}{M_1}$

5. Number of moles of sub compound $N_2 = \dfrac{\rho_2 V_2}{M_2}$

6. The mole fraction of the first liquid $X_1 = \dfrac{N_1}{N_1 + N_2}$

7. Mole fraction of the second liquid $X_2 = \dfrac{N_2}{N_1 + N_2}$

8. Mean molecular weight: $\overline{M} = M_1 X_1 + M_2 X_2$

9. Molar volumes of the liquids V_1 and V_2 $\qquad V_1 = \dfrac{M_1}{\rho_1}; \qquad V_2 = \dfrac{M_2}{\rho_2}$

10. Mean molar volume $\mathbf{V} = \dfrac{M}{\rho}$

11. Excess volume $V^E = V - (V_1 X_1 + V_2 X_2)$

  V = Experimental molar volume of the liquid mixture; V_1 = Mean molar volume of common compound
  V_2 = Mean molar volume of sub compound; $X1$ = Mole fraction of common compound; X_2 = Mole fraction of sub compound

12. Adiabatic compressibility $\beta_{ad} = \dfrac{1}{\rho U^2}$

  ρ = density of the liquid mixture; U = Velocity of the liquid mixture

13. Deviation in adiabatic compressibility $\Delta \boldsymbol{\beta_{ad}} = \beta_{ad} - (\beta_{ad\,1} X_1 + \beta_{ad\,2} X_2)$

  β_{ad} = Adiabatic compressibility of the liquid mixture ; $\beta_{ad\,1}$ = Adiabatic compressibility of the common compound ; $\beta_{ad\,2}$ = Adiabatic compressibility of the sub compound ; $X_1\ X_2$ are the mole fractions of common and sub compounds respectively

14. Molar sound velocity (or) Rao's constant: $R = \dfrac{\overline{M}}{\rho^{1/3}}$

15. Wada's constant: $W = \dfrac{\overline{M}}{\rho} \times \dfrac{1}{\beta^{1/7}}$

16. Inter molecular free length: $L_f = K (\beta_{ad})^{1/2}$; K = Jacobson's constant
  The values of K at the temperatures 30°C, 35°C, 40°C, 45°C are

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

17. Excess intermolecular free length: $L_f^E = L_{f\,mix} - (L_{f\,1} X_1 + L_{f\,2} X_2)$

  $L_{f\,mix}$ = experimental inter molecular free length of the liquid mixture; $L_{f\,1}$ = inter molecular free length of the common compound; $L_{f\,2}$ = inter molecular free length of the sub compound

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

  η_{mix} = experimental viscosity of the liquid mixture ; η_1 = viscosity of the common compound η_2 = viscosity of the sub compound

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

b = 2 and R = 8.3143

20. Excess internal pressure: $\pi^E = \pi_{real} - \pi_{ideal}$
21. Free volume: $V_f = (MV/K\eta)^{3/2}$
22. Excess free volume: $V_f^E = \mathbf{V_{f\ real}} - \mathbf{V_{f\ ideal}}$
23. Enthalpy: $H = \pi \cdot V_m$
24. Excess enthalpy: $H^E = H_{real} - H_{ideal}$
25. Excess Gibb's free energy: $G^E = RT\ [\ln \eta V - (X_1 \ln \eta_1 V_1 + X_2 \ln \eta_2 V_2)]$

        R = 1.987

Sound speed measurements have significance in science and technology since they provide valuable information about acoustic and thermodynamic parameters, the sign and magnitude of their excess functions being used to evaluate structure-making and /or structure-breaking effects arising due to mixing of two or more unlike liquids in varying proportions. We can apply different theoretical approaches of sound speed like the Nomoto Relation (NOM) and the Vandael Vangeel Ideal Mixing Relation (VAN) to the experimental sound speed to find the best suited theory for the system under investigation.

Using various theories ultrasonic sound velocities in liquid mixtures have been calculated and compared with experimental values. Comparison of theoretical values of ultrasonic velocities with those obtained experimentally in the present binary liquid mixtures is expected to reveal the nature of interaction between component molecules in the mixture. Such theoretical study is useful in finding the comprehensive theoretical model for the liquid mixtures. These ultrasonic sound velocities of liquid mixtures are valuable in testing various theories of liquid state. Theoretical evaluation of ultrasonic velocity in binary liquid mixtures and its correlation to study molecular interaction has been successfully done in recent years.

In recent years, the measurement of ultrasonic velocity has been adequately employed in understanding the nature of molecular interactions in pure liquids and liquid mixtures.

B. Theoretical considerations

1) Nomoto Equation

Rao[62] found experimentally that, for pure liquids, the ratio of temperature coefficients of sound velocity U and molar volume V remains almost constant:

$[(1/U)(dU/dT)] / [(1/V)(dV/dT)] = -3$

where T is the absolute temperature. Integrating this equation one obtains:

$$VU^{1/3} = \text{const} = M/\square\ \square\ U^{1/3} = R$$

where M is molecular weight and $\square$ is density. The constant R is called the molar sound velocity or Rao's constant. It was found to be additive i.e it can be calculated as a sum of increments from the atoms or atom groups in the molecule and from the chemical bonds.

On assuming the additivity of molar sound velocity (R) and no volume change on mixing, Nomoto established the following relation[6] for a liquid mixture

$$R = M/\square\ U^{1/3}$$

Where U and $\square$ are determined experimentally and M is the mean molecular weight in a binary liquid mixture

$$M = (X_1 M_1 + X_2 M_2)$$

Where M_1 and M_2 are molecular weights of constituent components.

Simple manipulation yields the following relation[6]

$$U_{Nomoto} = [(X_1 R_1 + X_2 R_2) / (X_1 V_1 + X_2 V_2)]^3$$

C. The Van Dael and Vangeel Equation

The ideal mixing theory advanced by Van Dael and Vangeel[7] in the light of assumptions made by Blandamer and Waddington[63], yield the following relation[64] for adiabatic compressibility $(\square_{ad})_{imx}$

$$(\square_{ad})_{imx} = \square_1 \square_1 / \square_{imx} (\square_{ad})_1 + \square_2\ \square_2 / \square_{imx} (\square_{ad})_2$$

where $\square_1$, $\square_2$ are the volume fraction of species 1 and 2, $\square_1$ and $\square_2$ are ratios of specific heats of the respective species. This relation holds well if the mixture is ideal and if $\square_1 = \square_2 = \square_{imx}$. Using the additional assumption that $V_1 = V_2$ the above equation can be transformed in to a linear combination of mole fraction X_1 and X_2.

$$(\square_{ad})_{imx} = X_1(\square_{ad})_1 + X_2(\square_{ad})_2$$

On the basis of this equation, Van Dael obtained the relation for ultrasonic velocity in liquid mixtures as

$$1/(X_1 M_1 + X_2 M_2) * 1/U^2_{imx} = X_1/M_1 U_1^2 + X_2/M_2 U_2^2$$

Where U_{imx} is the ideal mixing ultrasonic velocity in liquid mixture. U_1 and U_2 are ultrasonic velocities in species.

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