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Thermoacoustical and Excess Properties of Binary Mixtures of Ethyl Butyrate with Methanol and Vinyl Acetate

Shahla Parveen, Maimoona Yasmin, Manisha Gupta* and Jagdish Prasad Shukla

Department of Physics, Lucknow University, Lucknow-226007, India
*corresponding author: email: guptagm@rediffmail.com, shahla47@rediffmail.com

Abstract

This paper aims to portray the nature of interaction present in the mixture of ethyl butyrate with methanol and vinyl acetate by computing various thermodynamic parameters at 298.15 K. Excess thermodynamic properties correlated with Redlich–Kister polynomial equation reveals the extent of interaction present in the mixture. Acoustical relations giving the molecular radii of liquid mixtures suggest the change in structure with composition quite well. A comparative study of various empirical and semi-empirical relations such as Flory's Statistical Theory, Goldsack and Sarvas, Sanchez theory etc. for predicting ultrasonic velocity of the mixtures with the experimental values have been done.

Keywords: *Flory statistical theory, ultrasonic velocity, thermodynamic parameters, Sanchez theory.*

1. Introduction

Liquids and especially liquid mixtures are widely used in processing and product formulation in many industrial applications. Thermodynamic and transport properties of the liquids provide useful information about physical forces acting between the molecules of the same substance in pure liquids and molecules of different substances in liquid mixtures. When two liquids are mixed together, the resulting changes in physical and thermodynamic properties can be considered as a sum of several contributions due to free volume change, change in energy, change in molecular orientations, steric hindrances etc. Properties such as ultrasonic velocity or surface tension and their variation with temperature and composition of the binary mixture are useful to design engineering processes and in chemical and biological industries.

Vinyl acetate is a colourless liquid with pungent odour, it is a precursor to polyvinyl acetate, an important polymer in industry. Ethyl butyrate is used as artificial flavouring in alcoholic beverages, as a solvent in perfumery products and as a plasticizer for cellulose. Methanol, also known as methyl alcohol, carbinol, wood alcohol, wood naphtha or wood spirit, is a polar liquid at room temperature and is used as an antifreeze, solvent, fuel and as a denaturant for ethyl alcohol. It is also used for producing biodiesel via transesterification reaction.

The present paper reports the study of intermolecular interaction in the binary liquid mixture of ethyl butyrate with methanol (M+EB) and vinyl acetate (VA+EB) respectively at 298.15 K in terms of various thermodynamic and excess parameters. The surface tension of liquid mixtures is useful in the design of separation processes as it has significant effect on interface heat and mass transfer. Therefore, surface tension of binary liquid mixtures of ethyl butyrate with methanol and vinyl acetate respectively has been evaluated using Flory statistical theory (Flory 1965; Abe and Flory 1965).

The ultrasonic velocity of these mixtures are also analyzed in light of theoretical relations suggested by Van Deal and Vangeel, Nomoto, Junjie, Schaff's relation, Sanchez theory, Goldsack-Sarvas volume fraction statistics and Sudgen's relation, and the results have been compared with the experimental data.

The experimental data needed for the purpose have been taken from the literature (Resa *et al* 2002).

2. Theoretical Analysis

2.1. Debye temperature and heat capacity at constant pressure

The effective Debye temperature θ_D can be evaluated by using the following expression (Yasmin *et al* 2009).

$$\theta_D = \frac{h}{k}\left[\frac{9N}{4\pi V_m\left\{\left(\frac{1}{u_l^3}+\frac{2}{u_t^3}\right)\right\}}\right]^{1/3} \quad (1)$$

where u_l and u_t are the propagation velocities for longitudinal and transverse modes respectively. V_m is the molar volume and *h*, *k* and *N* are the Planck's constant, Boltzmann's constant and Avogadro's number respectively. The two wave velocities may be expressed in terms of density (ρ_m), the instantaneous adiabatic compressibility (k_s) and Poisson's ratio (σ) for liquids exhibiting the quasi-crystalline properties, as follows

$$\frac{1}{u_l^3}+\frac{2}{u_t^3} = (k_s\,\rho_m)^{3/2} \times \left[\left\{\frac{1+\sigma}{3(1-\sigma)}\right\}^{3/2} + 2\left\{\frac{2(1+\sigma)}{3(1-2\sigma)}\right\}^{3/2}\right] \quad (2)$$

where $k_s = 1/u^2\rho$

*Corresponding Author

and $$C_p = \frac{T\alpha^2 V}{k_T - k_s} \tag{3}$$

and α, k_T, C_P represent the coefficient of linear expansion, the isothermal compressibility and the specific heat at constant pressure respectively.

The Poisson's ratio is given by

$$\sigma = \frac{3A-2}{6A+2} \tag{4}$$

and

$$A = \frac{4}{3\ell} \tag{5}$$

where ℓ is the specific heat ratio.

2.2. Surface tension

According to Flory's statistical theory the surface tension is expressed as

$$\gamma_m = \gamma^* \tilde{\gamma}\left(\tilde{V}\right) \tag{6}$$

where γ^* and $\tilde{\gamma}$ ($\tilde{V}$) are the characteristic surface tension and reduced surface tension respectively. Patterson and Rastogi (1970) in their extension of the corresponding states theory to the case of surface tension obtained the following relations for characteristic and reduced surface tension

$$\gamma^* = k^{1/3} P^{*2/3} T^{*1/3} \tag{7}$$

$$\tilde{\gamma}\left(\tilde{V}\right) = M\tilde{V}^{-5/3} - \frac{\tilde{V}^{1/3} - 1}{\tilde{V}^2} \ell n \left[\frac{\tilde{V}^{1/3} - 0.5}{\tilde{V}^{1/3} - 1} \right] \tag{8}$$

Here k is Boltzmann constant, P^* and T^* are the characteristic pressure and temperature respectively. M is the fraction of nearest neighbours that a molecule loses on moving from the bulk of the liquid to the surface. Its most suitable value is 0.29 which is used in present calculation. $\tilde{V}$ is the reduced volume.

2.3. Excess parameters

Excess parameters, associated with a liquid mixture, are a quantitative measure of deviation in the behaviour of the liquid mixture from ideality. These functions are found to be sensitive towards the intermolecular forces and also on the difference in size and shape of the molecules. The literature survey (Prausnitz 1999) reveals that the most common way to evaluate the excess value of a given thermodynamic parameter is to use the equation

$$A^E = A_{\exp} - \sum_i x_i A_i \tag{9}$$

where A_{exp}, A_i, A^E and x_i are the experimentally measured value of the parameter A, value of parameter A for the i^{th} component, excess values of the parameter A, and mole fraction of i^{th} component.(i=1, 2 for binary mixture). A^E is excess isentropic compressibility (k_s^E), excess free length (L_f^E), excess acoustic impedance (Z^E), excess internal pressure (π_i^E) and excess Grüneisen parameter (Γ^E) as given below.

$$k_s^E = \frac{1}{u_m^2 \rho_m} - \left(\frac{x_1}{u_1^2 \rho_1} + \frac{x_2}{u_2^2 \rho_2} \right) \tag{9.1}$$

$$L_f^E = \frac{K}{(u_m^2 \rho_m)^{\frac{1}{2}}} - \left[\frac{x_1 K}{(u_1^2 \rho_1)^{\frac{1}{2}}} + \frac{x_2 K}{(u_2^2 \rho_2)^{\frac{1}{2}}} \right] \tag{9.2}$$

$$Z^E = (\rho_m u_m) - (x_1 \rho_1 u_1 + x_2 \rho_2 u_2) \tag{9.3}$$

$$\pi_i^E = \frac{\alpha T}{\beta_T} - \left(\frac{x_1 \alpha_1 T}{\beta_{T1}} + \frac{x_2 \alpha_2 T}{\beta_{T2}} \right) \tag{9.4}$$

$$\Gamma^E = \frac{\gamma - 1}{\alpha T} - \left(\frac{\gamma_1 - 1}{\alpha_1 T} + \frac{\gamma_2 - 1}{\alpha_2 T} \right) \tag{9.5}$$

Using the Flory theory, excess enthalpy (ΔH^{*E}) and excess free energy (ΔG^{*E}) (Abe and Flory 1965; Flory 1965) can be expressed as:

$$\Delta H^{*E} = \sum_{i=1}^{2} x_i P_i^* V_i^* \left(\frac{1}{\tilde{V}_i} - \frac{1}{\tilde{V}} \right) + \frac{x_1 \theta_2 V_1^* X_{12}}{\tilde{V}} \tag{10}$$

$$\begin{aligned} \Delta G^{*E} &= \sum_{i=1}^{2} x_i P_i^* V \times \\ &\left[\left(\frac{1}{\tilde{V}_i} - \frac{1}{\tilde{V}} \right) + 3\tilde{T}_i \ln \left(\frac{\tilde{V}_i^{1/3} - 1}{\tilde{V}^{1/3} - 1} \right) \right] + \frac{x_1 \theta_2 V_i^* X_{12}}{\tilde{V}} \end{aligned} \tag{11}$$

2.4. Redlich-Kister polynomial equation

The composition dependences of the excess properties are correlated by the Redlich-Kister polynomial equation (1984)

$$Y^E = x_1 \left(1 - x_1\right) \sum_{i=1}^{5} a_i \left(2x_1 - 1\right)^{i-1} \tag{12}$$

The values of the coefficient a_i were calculated by method of least squares along with the standard deviation $\sigma(Y^E)$. The coefficient a_i is adjustable parameters for a better fit of the excess functions.

The standard deviation values were obtained from the relation

$$\sigma\left(Y^E\right) = \left(\sum_{i=1}^{n} \left(Y_{exp}^E - Y_{cal}^E\right)^2 \Big/ (n-p) \right)^{1/2} \tag{13}$$

where n is the number of experimental points, p is the number of parameters, and Y_{expt} and Y_{cal} are the experimental and calculated parameters respectively.

2.5. Molecular radius

Ultrasonic techniques prove to be quite informative in structural measurements as the velocity of sound is much affected by the change in intermolecular distances. A few acoustic methods have been suggested by Schaff, Rao, and Kittel (Pandey et al. 2004). A modified form of Schaff's equation, without considering the effect of specific heat ratio on the constant 'b', has also been tested . Molecular radius has also been evaluated considering no free space between the molecules. The related equations are given below.

Molecular radius from the van der Waals constant 'b'

$$r=\left(\frac{3b}{16\pi N}\right)^{1/3} \tag{14}$$

'b' can be calculated using following equations:

Eyrings equation

$$b=\frac{2^{3/2}\pi}{3}V\left[1-\left\{1-\frac{1}{u}\left(\frac{\ell RT}{m}\right)^{1/2}\right\}^{3}\right] \tag{15}$$

Schaff's equation

$$b=V\left[1-\frac{\ell RT}{mu^{2}}\left\{\left(1+\frac{mu^{2}}{3\ell RT}\right)^{1/2}-1\right\}\right] \tag{16}$$

Rao's equation

$$b=V\left[1-\frac{\ell RT}{mu^{2}}\left\{\left(1+\frac{mu^{2}}{\ell RT}\right)^{1/2}-1\right\}\right] \tag{17}$$

Kittel's equation

$$b=\frac{(2)^{3/2}\pi}{3}V\left[1-\frac{1}{u}\left(\frac{3\ell RT}{m}\right)^{1/2}\right] \tag{18}$$

where ℓ is the specific heat ratio.

Equation without considering free space

$$r=\frac{1}{2^{5/6}}\left(\frac{V}{N}\right)^{1/3} \tag{19}$$

2.6. Ultrasonic velocity

According to Auerbach (1948) the ultrasonic velocity *(u)* is expressed by the relation

$$u=\left(\frac{\gamma}{6.3\times10^{-4}\rho}\right)^{2/3} \tag{20}$$

where γ and ρ are the surface tension and density in mN·m^{-1} and g·cm^{-1} respectively.

Furthermore four mixing rules viz. Van Deal and Vangeel, Nomoto, Junjie and Schaff's relation have been used to compute ultrasonic velocity theoretically described earlier (Shukla *et al* 2006).

Sanchez (1983) relation has been applied successfully to binary liquid mixtures to deduce the values of surface tension of liquid mixtures

$$\gamma=\sum_i\left(x_iA_i^{1/2}\right)\left[\sum_i\frac{(\phi_i\rho_i)}{(\phi_ik_{Ti})}\right]^{1/2} \tag{21}$$

where k_{Ti}, $\rho_{i,,}$ ϕ_i and x_i are the isothermal compressibilities, densities of pure liquids volume fraction and the mole fraction of the ith component. A_i is defined as

$$A_i=\gamma_i^{2}\left(\frac{k_{Ti}}{\rho_i}\right) \tag{22}$$

Goldsack and Sarvas (1981) used the mole fraction and volume fraction statistics to obtain the following expression for the surface tension of non-electrolyte solutions and applied this equation to obtain surface tension of various organic liquid mixtures.

$$\gamma=-\left(\frac{RT}{A}\right)\ln\left[x_1\exp\left(\frac{-\gamma_1A}{RT}\right)+x_2\exp\left(\frac{-\gamma_2A}{RT}\right)\right] \tag{23}$$

where A is the molar surface area.

According to Sudgen, (Reid *et al* 1976), γ can be obtained for a binary mixture as

$$\gamma=\left\{\sum_i[P_i]\frac{x_i}{M_i}\right\}^{4}\rho^{4} \tag{24}$$

and the parachor $[P_i]$ is given by

$$[P_i]=\gamma_i^{1/4}\left(\frac{M_i}{\rho_i}\right) \tag{25}$$

where M_i is the molar mass of the pure component $i(=1,2)$ and ρ is the density of the component.

3. Results And Discussion

The values of effective Debye temperature (θ_D), heat capacity (C_P) and surface tension *(γ)*, calculated from Eqns. 1, 3 and 6 for the mixture ethyl butyrate with methanol and vinyl acetate with mole fraction of ethyl butyrate (x_1) at T= 298.15 K are given in Table 1.

Thermodynamic parameters are diagnostic parameters for describing various properties of liquids and liquid mixtures. The derived parameters such as heat capacity (C_p), effective and Debye temperature (θ_D) give more comprehensive information about the structural and interactional aspects of the mixture at the microscopic level. A close perusal of Table 1 reveals that the value of effective Debye temperature (θ_D) increases with increase in composition for both the mixtures, whereas heat capacity (C_p) decreases. Both the parameters increase linearly with mole fraction.

Table 1. Calculated Values of Debye Temperature θ_D, Heat Capacity At Constant Pressure C_p and Surface Tension γ for the Binary Mixture of Methanol + Ethyl Butyrate and Vinyl Acetate + Ethyl Butyrate at 298.15 K.

x_2	θ_D	C_p cal.mol^{-1}	γ mNm^{-1}
Methanol + Ethyl Butyrate			
1.000	54.779	169.900	22.589
0.902	55.979	157.324	22.468
0.806	57.218	144.901	22.324
0.693	58.809	130.250	22.121
0.607	60.156	119.136	21.942
0.497	62.086	104.966	21.669
0.396	64.116	92.016	21.363
0.296	66.425	79.246	20.984
0.198	69.076	66.815	20.510
0.100	72.235	54.484	19.883
0.000	76.267	42.085	18.992
Vinyl Acetate + Ethyl Butyrate			
1.000	54.779	169.900	22.356
0.917	55.040	165.902	22.353
0.809	55.398	160.742	22.352
0.693	55.800	155.232	22.354
0.591	56.171	150.418	22.359
0.503	56.503	146.284	22.366
0.406	56.878	141.733	22.376
0.307	57.281	137.127	22.390
0.193	57.780	131.882	22.415
0.101	58.205	127.681	22.440
0.000	58.702	123.119	22.476

Surface tension *(γ)* of the mixture decreases gradually for the mixture M+EB while for VA+EB it first decreases with decreasing mole fraction of ethyl butyrate and then increases with decreasing mole fraction of ethyl butyrate. This indicates the presence of dispersive forces near x_2=0.809 which is responsible for the decrease in surface tension.

Excess properties provide information about the molecular interactions and macroscopic behaviour of fluid mixtures and can be used to test and improve thermodynamic models for calculating and predicting the fluid phase equilibria.

The excess isentropic compressibility (k_s^E), excess free length (L_f^E), excess acoustic impedance (Z^E), excess enthalpy(ΔH^{*E}), excess free energy (ΔG^{*E}), excess internal pressure (π_i^E) and excess Grüneisen parameter (Γ^E) of the two binary mixtures viz. (M+EB) and (VA+EB) have been computed and correlated with Redlic-Kister polynomial equation at 298.15 K. The values of coefficient a_i evaluated using the method of least squares for both the mixtures are given in Table 2 along with the standard deviations $\sigma(Y^E)$. These parameters help us in providing an in depth picture of various interactions between the component. Variation of these excess properties with mole fraction of ethyl butyrate for both the mixture are given in Figures 1-7.

The excess isentropic compressibility (k_s^E) and excess intermolecular free length (L_f^E) are found to be negative for the binary mixture of M+EB and very less positive for VA+EB (Figures 1 and 2). The negative values of k_s^E and L_f^E show that there exists a strong intermolecular interaction between methanol and ethyl butyrate molecules, however positive values of k_s^E and L_f^E for the system VA+EB indicate the presence of comparatively less intermolecular interaction between the two components. Similar variations in excess molar volume and change of speed of sound with mole fraction of ethyl butyrate for the systems M+EB and VA+EB have been found by Resa et al (2002).

Table 2. Adjustable Parameters a_i With The Standard Deviations $\sigma(Y^E)$ For Excess Isentropic Compressibility k_s^E, Excess Acoustic Impedance Z^E , Excess Free Length L_f^E, Excess Enthalpy ΔH^{*E}, Excess Gibb's Free Energy ΔG^{*E}, Excess Internal Pressure $\Pi^E{}_i$, And Excess Pseudo-Grüneisen Parameter Γ^E, For Both The Binary Mixtures At 298.15 K.

Parameter	a_1	a_2	a_3	a_4	a_5	$\sigma(Y^E)$
Methanol + Ethyl Butyrate						
k_s^E [×10^{10} N^{-1}m^2]	-2.3055	1.1859	-.6999	0.0979	0.0030	0.0093
Z^E[×10^{-4}kg.m^{-2}.s^{-1}]	15.179	-7.1173	4.1724	-0.9581	0.2971	0.0059
L_f^E [A°]	-7.1677	3.6587	-1.9775	-0.0017	-1.7401	0.0277
ΔH^{*E} [kJmol^{-1}]	0.246	-0.0924	0.0134	-0.0418	0.0195	0.0001
ΔG^{*E} [kJmol^{-1}]	0.264	-0.0967	0.0366	-0.027	-0.0043	0.0011
π_i^E[× 10^{-8} Nm^{-2}]	5.1256	-2.2671	1.3572	-0.2473	0.1553	0.0022
Γ^E	-0.0549	0.0874	0.0053	-0.0747	-0.1011	0.0000
Vinyl Acetate + Ethyl Butyrate						
k_s^E [×10^{10} N^{-1}m^2]	0.2424	-0.1472	-0.2168	-0.0175	1.3264	0.0049
Z^E[×10^{-4}kg.m^{-2}.s $^{-1}$]	-1.3012	0.1081	0.2315	0.4870	-0.8527	0.0303
L_f^E [A°]	0.0924	-0.0396	-0.0574	-0.0314	0.4164	0.0016
ΔH^{*E} [kJmol^{-1}]	0.1814	-0.0239	-0.0022	0.0079	0.0200	0.0001
ΔG^{*E} [kJmol^{-1}]	0.1517	-0.0179	0.0016	-0.0011	0.0009	0.0000
π_i^E[× 10^{-8} Nm^{-2}]	-0.2454	0.0579	0.0373	0.0230	-0.3227	0.0014
Γ^E	0.0232	-0.1891	-0.8134	-1.1560	-0.5380	0.0001

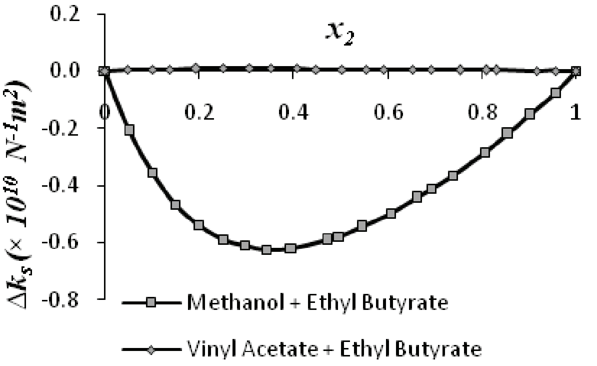

Figure 1. Excess isentropic compressibility (k_s^E) vs. mole fraction of ethyl butyrate (x_2) for binary mixtures methanol + ethyl butyrate and vinyl acetate + ethyl butyrate at 298.15K.

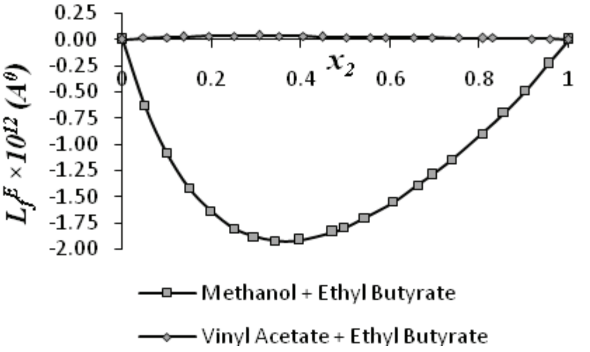

Figure 2. Excess intermolecular free length (L_f^E) vs .mole fraction of ethyl butyrate (x_2) for binary mixtures methanol + ethyl butyrate and vinyl acetate + ethyl butyrate at 298.15 K.

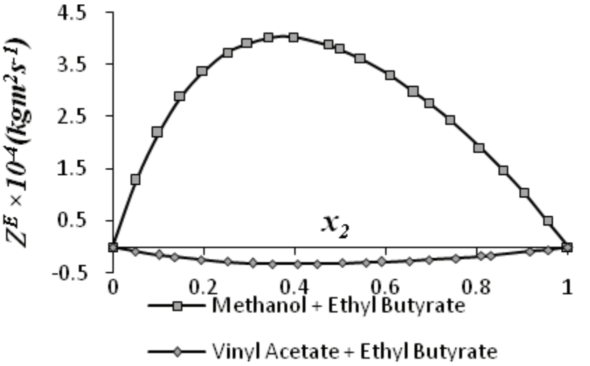

Figure 3. Excess acoustic impedance (Z^E)vs. mole fraction of ethyl butyrate (x_2) for binary mixtures methanol+ethyl butyrate and vinyl acetate + ethyl butyrate at 298.15 K.

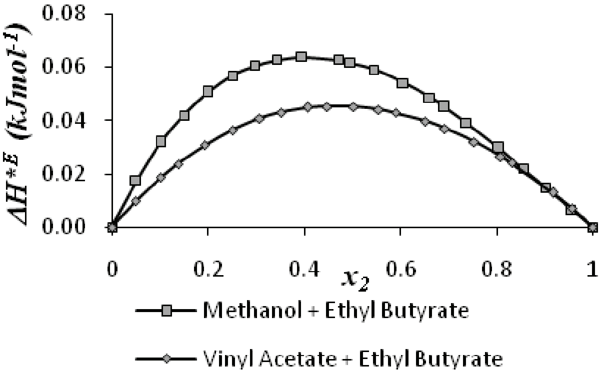

Figure 4. Excess molar enthalpy (ΔH^{*E})vs. mole fraction of ethyl butyrate (x_2) for binary mixtures methanol + ethyl butyrate and vinyl acetate + ethyl butyrate at 298.15 K.

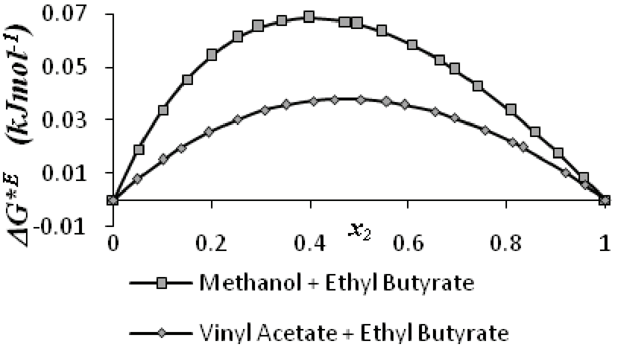

Figure 5. Excess Gibb's free energy of activation for viscous flow (ΔG^{*E}) vs. mole fraction of ethyl butyrate (x_2) for binary mixtures methanol + ethyl butyrate and vinyl acetate + ethyl butyrate at 298.15 K.

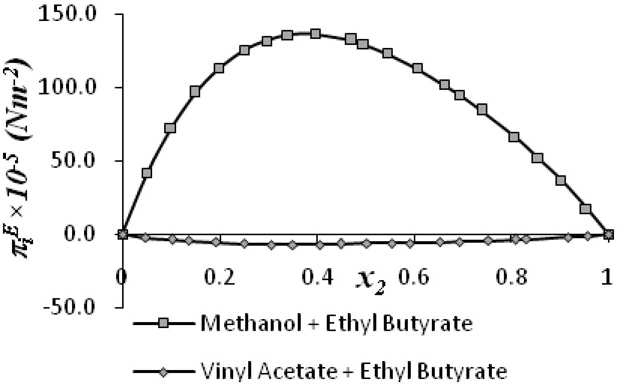

Figure 6. Excess internal pressure (π_i^E) vs. mole fraction of ethyl butyrate (x_2) for binary mixtures methanol+ethyl butyrate and vinyl acetate + ethyl butyrate at 298.15 K.

Specific acoustic impedance is a quantity, which depends on the molecular packing of the systems. Excess acoustic impedance (Z^E) is positive for M+EB and small negative for VA+EB mixtures (Figure 3). The positive values of Z^E in M+EB system reflect the strong interaction in comparison with VA+EB system. The observed positive values (Figures 4 and 5) of excess enthalpy ΔH^{*E} and excess Gibbs free energy ΔG^{*E} can be interpreted in terms of intermolecular interaction through hydrogen bonding. Maham et al (2002) have reported similar variations in excess Gibbs free energy behaviour for aqueous solutions of ethanolamine.

The role of internal pressure in solution thermodynamics was recognized many years ago by Hilderband following earlier work of Van Laar (Prausnitz 1969). It has been found to be an important tool in the study of several chemical reactions and in the investigation of molecular interaction (Pandey *et al* 2003). The values of excess internal pressure (π^E_i) are found to be positive for the binary mixtures of M+EB and negative for the mixture of VA+EB over the entire mole fraction range (Figure 6). This further supports the view that intermolecular interaction is stronger in VA+EB mixture.

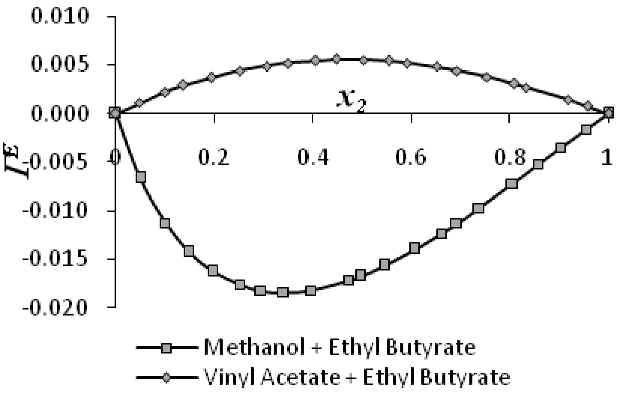

Figure 7. Excess pseudo Grüneisen parameter vs. mole fraction of ethyl butyrate (x_2) for binary mixtures methanol + ethyl butyrate and vinyl acetate + ethyl butyrate at 298.15 K.

Grüneisen parameter *(Γ)* is one of the important parameters which is used to study internal structure clustering phenomenon and thermodynamic properties of solid crystalline lattice. It is well established that liquids support a quasi-crystalline model for their structure, the lattice nature being increased at high pressure and low temperature and the Grüneisen parameter can also be used to study them. It is also evident from Figure 7, that the values of excess Grüneisen parameter *(Γ^E)* for the binary mixture of M+EB are negative. The negative values of Γ^E show that there exists a strong specific interaction between methanol and ethyl butyrate molecules leading to the formation of molecular complex between the two species in the liquid state.

The positive values of Γ^E for the system VA+EB are an indication of comparatively weak interaction between the components of binary liquids mixtures (Yasmin *et al* 2009).

The study of variation of molecular radius with composition of liquid mixtures offers an indirect but convenient way to ascertain the structural arrangement, nature and possibilities of microscopic interactions between the like as well as unlike species.

As can be seen from the Figure 8(a) and 8(b), there is a considerable change in molecular radius *(r)* with composition for M+EB system while the change is very small for VA+EB. It is large in ethyl butyrate rich region and gradually decreases with decreasing mole fraction of ethyl butyrate. The variation of molecular radius with mole fraction of ethyl butyrate is not exactly linear in case of M+EB. This may be because of the hydrogen bonding between the two species resulting in comparatively larger molecules. While in case of VA+EB the variation is exactly linear showing less interaction on mixing. The smaller entities occupying smaller volume cause a compact arrangement giving smaller values of radii.

Further ultrasonic velocities calculated theoretically using Van Deal and Vangeel, Nomoto, Junjie, Schaff's relation, Flory's Statistical Theory Sanchez theory, Goldsack-Sarvas volume fraction statistics and Sudgen's relation for M+EB and VA+EB systems have been shown with the experimental values and shown in Figures 9(a) and (b). It is observed from Table 3 that ultrasonic velocity using Nomoto, Junjie and Schaff's relation is deviating very less from the experimental values for the binary mixtures followed by FST. The small deviation indicates the applicability of the theory for computing the ultrasonic velocity of these binary liquid mixtures. Van Deal and Vangeel (VDVG) and Sudgen's relation show larger deviations for the mixture M+EB. Deviations in ultrasonic velocity using Goldsack and Sarvas (GS) and Sanchez relations are also within the limits of error.

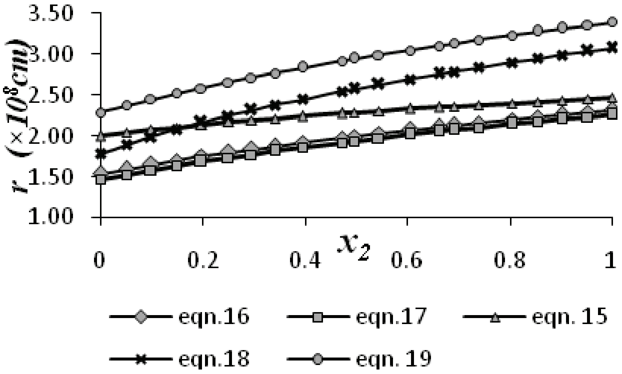

Figure 8(a). Molecular radius vs. mole fraction of ethyl butyrate (x_2) for binary mixture of methanol + ethyl butyrate at 298.15 K.

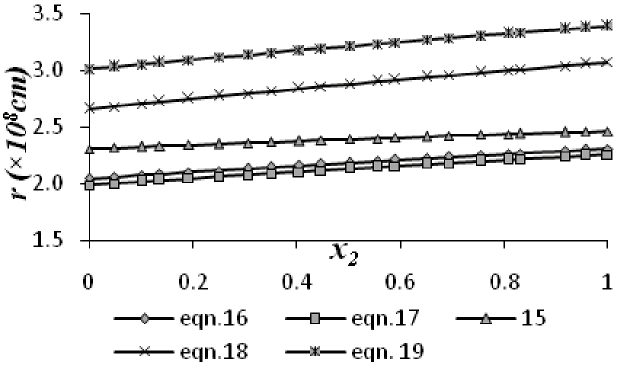

Figure 8(b). Molecular radius vs. mole fraction of ethyl butyrate (x_2) for binary mixture of vinyl acetate + ethyl butyrate at 298.15 K.

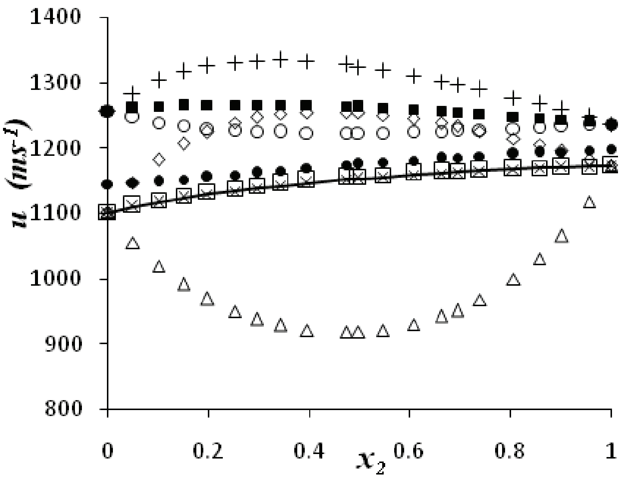

Figure 9(a). Ultrasonic velocity vs. mole fraction of ethyl butyrate (x_2) for binary mixture of methanol + ethyl butyrate at 298.15 K, using (Δ)Van Deal and Vangeel, (□)Nomoto, (×) Junjie, (◊)Schaff's relation (●)Flory's Statistical Theory (■)Sanchez theory, (o)Goldsack-Sarvas, (+)Sudgen's relation(—) and experimental values.

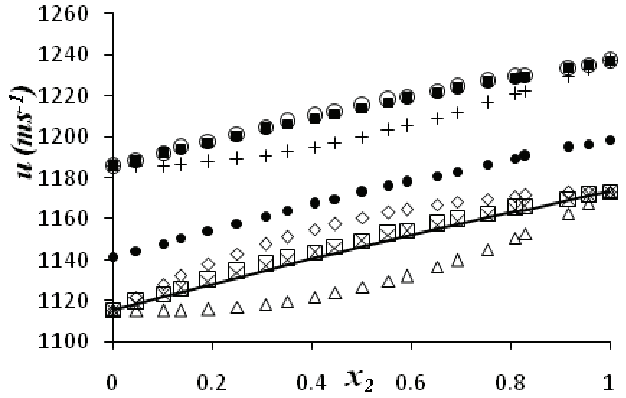

Figure 9(b). Ultrasonic velocity vs. mole fraction of ethyl butyrate (x_2) for binary mixture of vinyl acetate + ethyl butyrate at 298.15 K, using (Δ)Van Deal and Vangeel, (□)Nomoto, (×) Junjie, (◊)Schaff's relation (●)Flory's Statistical Theory (■)Sanchez theory, (O)Goldsack-Sarvas, (+)Sudgen's relation(—) and experimental values..

Table 3.Average Percentage Deviations In The Calculated Values Of The Ultrasonic Velocity With The Experimentally Measured Values.

Theory	APD		Theory	APD	
	M+EB	VA+EB		M+ EB	VA+EB
VDVG	13.63	1.10	Sanchez	-9.55	-5.88
Nomoto	0.21	0.16	GS	-7.29	-5.94
Junjie	0.00	0.15	Sudgen	-13.19	-5.10
Shaaff	-0.82	-0.13	Flory	2.10	-1.49

4. Conclusion

The computed parameters predict the nature of interaction in the mixture quite successfully. The observed values of thermodynamic and excess parameters for both the mixtures show that the molecular interaction is stronger in the binary mixture of M+EB. The system VA+EB shows the ideal behavior whereas the system M+ EB deviates much from ideality. There is a good agreement between the results concluded from the calculated data in this paper and the results mentioned in the paper from where the data has been taken. The study of molecular radius also throws some light on the change in structural arrangement of the system on mixing. Further the theories used for estimation of velocities show good agreement with the respective measured values of ultrasonic velocity.

Nomenclature

b	van der Waal's constant
C_p	Heat Capacity at Constant Pressure in cal·mol^{-1}
h	Planck's constant
k	Boltzmann's constant
k_s^E	Excess Isentropic Compressibility in N^{-1}·m^2
k_T	Isothermal Compressibility in N^{-1}·m^2
k_{Ti}	Isothermal compressibilities in N^{-1}·m^2
L_f^e	Excess Free Length in A^o
N	Avogadro's number
P^*	Characteristic Parameter
R	Molecular radius in m
T	Absolute temperature in K
T^*	Characteristic Parameter
u	Ultrasonic velocity in m·s^{-1}
V	Molar Volume in m^3·mol^{-1}
V^*	Characteristic Parameter
x_i	Mole fraction
Z^E	Excess Acoustic Impedance in kg·m^{-2}·s^{-1}
α	Thermal Expansion Coefficient in K^{-1}
ΔG^{*E}	Excess Free Energy in kJ·mol^{-1}
ΔH^{*E}	Excess Enthalpy in kJ·mol^{-1}
ℓ	Specific Heat Ratio
Γ^E	Excess Pseudo-Grüneisen Parameter
θ_D	Debye Temperature in Kelvin
$\rho_{i,}$	Densities of pure liquids in g·cm^{-3}
$\sigma(Y^E)$	Standard Deviations
σ	Poisson Ratio
APD	average percentage deviation

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