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

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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 provides useful information about physical forces acting between the molecules of the same substance in pure liquids and molecules of different substances in liquid mixtures. The effective Debye temperature \( \theta_D \) can be evaluated by using the following expression (Yasmin et al 2009).

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

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 can be expressed in terms of density (\( \rho_m \)), the instantaneous adiabatic compressibility (\( k_s \)) and Poisson’s ratio (\( \sigma \)) for liquids exhibiting the quasi-crystalline properties, as follows

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

where \( k_s = 1/\rho^2 \)
and \( C_p = \frac{T \alpha^2 V}{k_f - k_s} \) \hspace{1cm} (3)

and \( \alpha, k_f, C_p \) represent the coefficient of linear expansion, the isothermal compressibility and the specific heat at constant pressure respectively.

The Poisson’s ratio is given by

\[
\sigma = \frac{3A - 2}{6A + 2}
\]

(4)

and

\[
A = \frac{4}{3} \ell
\]

(5)

where \( \ell \) is the specific heat ratio.

### 2.2. Surface tension

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

\[
\gamma_m = \gamma^* \tilde{\gamma}(\tilde{V})
\]

(6)

where \( \gamma^* \) 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

\[
\gamma^* = k^{1/3}P^{2/3}T^{1/3}
\]

(7)

\[
\tilde{\gamma}(\tilde{V}) = M\tilde{V}^{-5/3} - \frac{\tilde{V}^{1/3} - 1}{\tilde{V}^{1/3} - 0.5}\ln\left[\frac{\tilde{V}^{1/3} - 0.5}{\tilde{V}^{1/3} - 1}\right]
\]

(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

\[
A^E = A_{exp} - \sum_i x_i A_i
\]

(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 \( (k_i^E) \), excess free length \( (L_i^E) \), excess acoustic impedance \( (Z_i^E) \), excess internal pressure \( (\pi_i^E) \) and excess Grüneisen parameter \( (\Gamma_i^E) \) as given below.

\[
k_i^E = \frac{L}{u_m \rho_m} - \left( \frac{x_1}{u_1^f \rho_1} + \frac{x_2}{u_2^f \rho_2} \right)
\]

(9.1)

\[
L_i^E = \frac{K}{(u_m^2 \rho_m)^{2/3}} \left[ \frac{x_1K}{(u_1^f \rho_1)^{2/3}} + \frac{x_2K}{(u_2^f \rho_2)^{2/3}} \right]
\]

(9.2)

\[
Z_i^E = (\rho m u_m) - (x_1 p_1 u_1 + x_2 p_2 u_2)
\]

(9.3)

\[
\pi_i^E = \frac{\alpha T}{\beta T} - \left( \frac{x_1 \alpha_1 T^2}{\beta_1 T_1} + \frac{x_2 \alpha_2 T^2}{\beta_2 T_2} \right)
\]

(9.4)

\[
\Gamma_i^E = \frac{\gamma - 1}{\alpha T} - \left( \frac{\gamma_1 - 1}{\alpha_1 T} + \frac{\gamma_2 - 1}{\alpha_2 T} \right)
\]

(9.5)

Using the Flory theory, excess enthalpy \( (\Delta H^E) \) and excess free energy \( (\Delta G^E) \) (Abe and Flory 1965; Flory 1965) can be expressed as:

\[
\Delta H^E = \sum_{i=1}^{2} x_i P_i^* V_i \left( \frac{1}{V_i} - \frac{1}{V} \right) + \frac{x_i \theta_j V_j^* X_{j2}}{V}
\]

(10)

\[
\Delta G^E = \sum_{i=1}^{2} x_i P_i^* V_i \times \left[ \frac{1}{V_i} - \frac{1}{V} \right] + 3 \sum_i x_i \theta_j V_j^* X_{j2} \ln \left( \frac{V_i^{1/3} - 1}{V^{1/3} - 1} \right) + \frac{x_i \theta_j V_j^* X_{j2}}{V}
\]

(11)

### 2.4. Redlich-Kister polynomial equation

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

\[
Y^E = (1 - x_j) \sum_{i=1}^{5} a_i (2x_j - 1)^{i-1}
\]

(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

\[
\sigma(Y^E) = \left( \sum_{i=1}^{n} \left( Y_{exp} - Y_{cal} \right)^2 \right)^{1/2} \left( n - p \right)
\]

(13)

where \( n \) is the number of experimental points, \( p \) is the number of parameters, and \( Y_{exp} \) 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’

\[ r = \left( \frac{3b}{16\pi N} \right)^{\frac{1}{3}} \]  

(14)

‘b’ can be calculated using following equations:

Eyring’s equation

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

(15)

Schaff’s equation

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

(16)

Rao’s equation

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

(17)

Kittel’s equation

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

(18)

where \( \ell \) is the specific heat ratio.

Equation without considering free space

\[ r = \frac{1}{2.5^{\frac{1}{3}}} \left[ \frac{V}{N} \right]^{\frac{1}{3}} \]  

(19)

2.6. Ultrasonic velocity

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

\[ u = \left( \frac{\gamma}{6.3 \times 10^{-4} \rho} \right)^{2/3} \]  

(20)

where \( \gamma \) and \( \rho \) are the surface tension and density in mN·m\(^{-1}\) and g·cm\(^{-1}\) respectively.

Furthermore four mixing rules viz. Van Deel 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

\[ \gamma = \sum_{i} \left( x_i A_i \right)^{1/2} \left[ \sum_{i} \left( \frac{\phi_i}{\phi_i K_i} \right) \right]^{1/2} \]  

(21)

where \( K_i, \rho_i, \phi_i \) and \( x_i \) are the isothermal compressibilities, densities of pure liquids volume fraction and the mole fraction of the \( i \)th component. \( A_i \) is defined as

\[ A_i = \gamma_i^2 \left( \frac{K_i}{\rho_i} \right) \]  

(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.

\[ \gamma = \left( \frac{RT}{A} \right) \ln \left[ x_1 \exp \left( \frac{-\gamma_1 A}{RT} \right) + x_2 \exp \left( \frac{-\gamma_2 A}{RT} \right) \right] \]  

(23)

where \( A \) is the molar surface area.

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

\[ \gamma = \left( \sum [P_i x_i] \right)^4 \rho^4 \]  

(24)

and the parachor \([P_i]\) is given by

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

(25)

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

3. Results And Discussion

The values of effective Debye temperature (\( \theta_D \)), heat capacity (\( C_P \)) and surface tension (\( \gamma \)), calculated from Eqns. 1, 3 and 6 for the mixture ethyl butyrate with methanol and vinyl acetate with mole fraction of ethyl butyrate (\( x_i \)) at \( T = 298.15 \text{ K} \) 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 (\( \theta_D \)) 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 (\( \theta_D \)) increases with increase in composition for both the mixtures, whereas heat capacity (\( C_P \)) decreases. Both the parameters increase linearly with mole fraction.
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 ($\Delta$)Van Deel and Vangeel, (□)Nomoto, ($\times$) Junjie, (◊)Schaff's relation (●)Flory's Statistical Theory (■)Sanchez theory, (ο)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.

<table>
<thead>
<tr>
<th>Theory</th>
<th>APD M+EB</th>
<th>VA+EB</th>
<th>Theory</th>
<th>APD M+EB</th>
<th>VA+EB</th>
</tr>
</thead>
<tbody>
<tr>
<td>VDVG</td>
<td>13.63</td>
<td>1.10</td>
<td>Sanchez</td>
<td>9.55</td>
<td>5.88</td>
</tr>
<tr>
<td>Nomoto</td>
<td>0.21</td>
<td>0.16</td>
<td>GS</td>
<td>7.29</td>
<td>5.94</td>
</tr>
<tr>
<td>Junjie</td>
<td>0.00</td>
<td>0.15</td>
<td>Sudgen</td>
<td>13.19</td>
<td>5.10</td>
</tr>
<tr>
<td>Shaaff</td>
<td>-0.82</td>
<td>-0.13</td>
<td>Flory</td>
<td>2.10</td>
<td>1.49</td>
</tr>
</tbody>
</table>

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
- $k_i$: Excess Isentropic Compressibility in N$^{-1}$·m$^2$
- $k_T$: Isothermal Compressibility in N$^{-1}$·m$^2$
- $k_{TT}$: Isothermal compressibilities in N$^{-1}$·m$^2$
- $L_f$: Excess Free Length in Å
- $N$: 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$^{-1}$
- $\alpha$: Thermal Expansion Coefficient in K$^{-1}$
- $\Delta G^*_{E}$: Excess Free Energy in kJ·mol$^{-1}$
- $\Delta H^*_{E}$: Excess Enthalpy in kJ·mol$^{-1}$
- $\iota$: Specific Heat Ratio
- $l^*$: Excess Pseudo-Grüneisen Parameter
- $\theta_{D}$: Debye Temperature in Kelvin
- $\rho_i$: Densities of pure liquids in g·cm$^{-3}$
- $\sigma$: Poisson Ratio
- $\sigma$: Standard Deviations
- APD: average percentage deviation

References:


Redlich, O., Kister, A.T., 1984, “Thermodynamics of Nonelectrolytic Solutions. Algebraic Representation of


