

# Excess internal pressure and excess enthalpies of some binary liquid mixtures of Ethyl Acetate with alkanols (C<sub>1</sub>-C<sub>4</sub>) at 298.15K, 303.15K and 308.15K

K. B. Bhamare

M. G. Vidyamandir's L. V. H. arts, science and commerce college, Nashik-03

## Abstract:

Internal pressure and enthalpies have been calculated from observed ultrasonic velocities, densities and viscosities of binary mixtures of ethyl acetate with methanol, ethanol, 1-propanol, 2-propanol, t-butanol, at 298.15 K, 303.15 K and 308.15 K. The calculated excess internal pressure and enthalpy have been used to discuss the results in terms of intermolecular interactions between the components of binary liquid mixtures.

## Introduction

Internal pressure ( $\pi$ ) is a fundamental property of liquid. It is a measure of cohesive forces acting in a liquid. It gives the resultant forces of attraction and repulsion between molecules. Therefore, many workers extended internal pressure studies to binary, ternary multi component liquid mixtures to predict intermolecular interactions. Enthalpy (H) of liquid is related to its internal pressure. Hence in the recent past many researchers studied excess internal pressure and excess enthalpy of mixture of liquid molecules to understand molecular processes [1-5].

A survey of the literature indicates that, studies of excess thermodynamic parameters such as excess internal pressure ( $\pi^E$ ) and excess enthalpy ( $H^E$ ) in order to understand the molecular interaction in binary mixtures of ethyl acetate with alkanols (C<sub>1</sub>-C<sub>4</sub>) are not done so far. Therefore internal pressure and enthalpy studies of these systems are made by measuring ultrasonic velocities, viscosities and densities of these binary mixtures. Since internal pressure of a liquid is sensitive to temperature, concentration and external pressure, studies are made on mixture of ethyl acetate with alkanols (C<sub>1</sub>-C<sub>4</sub>) over entire composition range and at various temperatures [6,7].

## Materials and methods:

The methods of measuring density, viscosity and ultrasonic velocity were same as earlier [8-10]. Ultrasonic velocity, viscosity and density of these mixtures have been measured in a thermostatic water bath of thermal stability  $\pm 0.01$  K using Mittal's F-18 ultrasonic interferometer operating at a fixed frequency of 2 MHz, Ostwald viscometer and bi-capillary pycnometer with an accuracy of  $\pm 0.03\%$ ,  $\pm 0.1\%$  respectively. The flow time for viscosity measurement were measured with a stopwatch correct to 0.01 second. All liquids were used after purification. The purity of liquid was checked by a comparing their experimental density values [11, 12]. Liquid mixtures over entire composition range were prepared in glass stopper bottle by mixing accurately weighted amount of ester and alkanols. Every care was taken to avoid contamination and evaporation during mixing. The accuracy in mole fraction was better than  $10^{-4}$ .

## Results:

The internal pressure of the liquids and liquid mixtures are obtained using the experimental ultrasonic velocity (U), density ( $\rho$ ) and viscosity ( $\eta$ ) using equation [13]:

$$\pi_i = bRT \left[ \frac{k\eta}{U} \right]^{1/2} \frac{\rho^{2/3}}{M^{7/6}} \quad (1)$$

where  $\pi_i$  is internal pressure, b stands for the cubic packing which is assumed to be 2 for all liquids and solutions, k the temperature independent constant =  $4.28 \times 10^9$ , R is gas constant. U is ultrasonic velocity,  $\eta$  is viscosity, T is absolute temperature,  $\rho$  is density of liquid and M is molecular weight of liquid. For liquid mixtures M is replaced by average molecular weight as,

$$M = M_1X_1 + M_2X_2 \quad (2)$$

In above equation,  $M_1$ ,  $X_1$  and  $M_2$ ,  $X_2$  are molecular weight and mole fraction of components 1 and 2 of liquid mixture. Enthalpies (H) of liquids are calculated by using the equation

$$H_i = \pi_i v_i \quad (3)$$

In above equation  $v_i$  is molar volume of liquid.

The excess internal pressure and enthalpy of binary liquid mixtures are obtained using the following equations:

$$\pi^E = \pi_{(mix)} - (X_1\pi_1 + X_2\pi_2) \quad (4)$$

and

$$H^E = \pi_{(\text{mix})} V_{(\text{mix})} - (X_1\pi_1V_1 + X_2\pi_2V_2) \quad (5)$$

Symbols of equations (4) and (5) have their usual meaning.

The variation of  $\pi^E$  and  $H^E$  with mole fraction of ethyl acetate ( $X_1$ ) at 298.15 K is shown in figure 1 and 2 respectively. Similar plots are obtained at other temperatures.

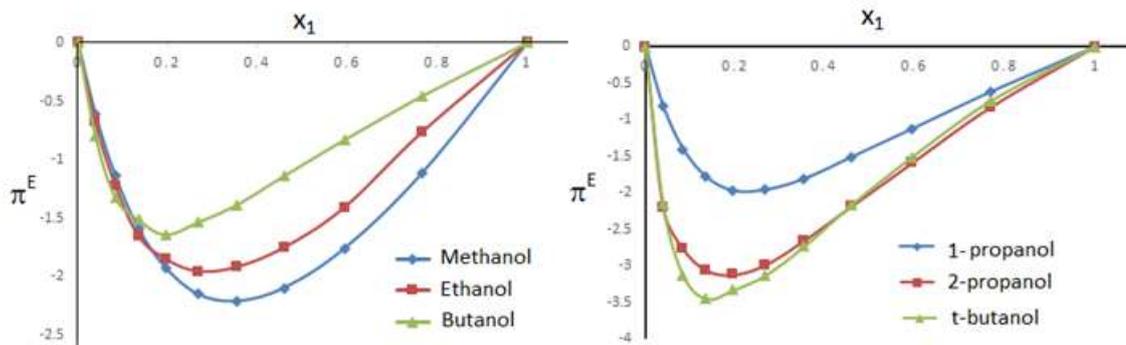


Figure 1: Variation of  $\pi^E$  with mole fraction ( $X_1$ )

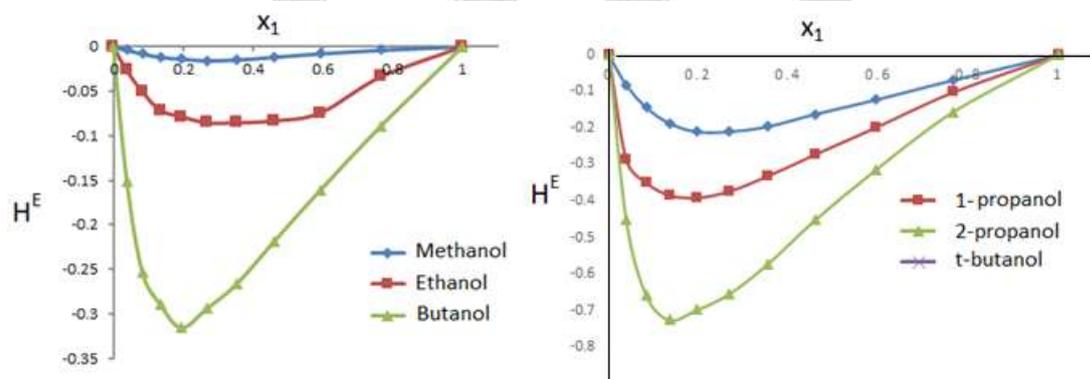


Figure 2: Variation of enthalpy ( $H^E$ ) with mole fraction ( $X_1$ ) of ethyl acetate.

### Discussions and conclusion:

The calculated internal pressure and enthalpy in all binary mixtures decreases with addition of ethyl acetate. Ester is proton acceptor, weakly polar and non-associating in nature [14]. Alkanols pure state or associated through hydrogen bonding [15]. When a small quantity of ester is added, the alkanols clusters are broken, resulting in dense packing of molecules inside the shield, which is responsible for the continuous decrease in internal pressure and enthalpy values in all binary mixtures. This process of declustering of alkanols with the addition of ester takes place rapidly at higher temperatures. Therefore, lower values of internal pressure and enthalpy are observed at higher temperatures. Excess internal pressure values of all binary mixtures are negative suggesting weak intermolecular interactions (figure 1).  $\pi^E$  values of n-alkanols follow the order as methanol > ethanol > propan-1-ol > butan-1-ol. This suggests that intermolecular interaction decreases with chain length of alkanols, probably due to less proton donating tendency of higher alkanols. Similarly branched alkanols have lower values of  $\pi^E$  than their straight chain homologues. This suggests that branched alkanols render more steric hindrance towards intermolecular interactions [16].

The observed  $H^E$  values may be analysed in terms of the formation of intermolecular hydrogen bonding and the breaking of associated structure of the alkanols. The  $H^E$  values are negative in all binary mixtures (figure 2) indicating the presence of exothermic molecular interactions through dipole-dipole interactions between free electrons of carboxylic group and proton from alkanols. The low values of  $H^E$  in higher and branched alkanols may be due to the weaker self-association and breaking up of alkanols structure on addition of ester. The higher values of  $H^E$  in lower alkanols may be interpreted in terms of higher tendency of complex formation between the molecules.

### References:

1. S. Oswal, 'Excess molar volumes of binary mixtures of alkanols with ethyl acetate from 298.15 to 323.15 K', *Thermochimica Acta* 373(2) 2001:141-152
2. Hamid Reza Rafiee, 'Volumetric properties for binary mixtures of ethyl acetate, vinyl acetate and tert-butyl acetate with 1-propanol and iso-butanol at T= (293.15–313.15) K and P=0.087Mpa', *Journal of Molecular Liquids* 213 (2015) :255-267
3. Ana B. Pereiro, 'Mixing properties of binary mixtures presenting azeotropes at several temperatures', *The Journal of Chemical Thermodynamics* 39(9) (2007) :1219-1230
4. Nicole Vieira, 'Fluorination effects on the thermodynamic, thermophysical and surface properties of ionic liquids', *The Journal of Chemical Thermodynamics* 97 (2015)
5. F.S. Teixeira, 'Phase equilibria and surfactant behavior of fluorinated ionic liquids with water', *The Journal of Chemical Thermodynamics* 82 (2015) 99–107.

6. Nakajima Toshio, Komatsu Tsuyoshi, Apparent Molal Volumes and Adiabatic Compressibilities of n-Alkanols and  $\alpha$ ,  $\omega$ -Alkane Diols in Dilute Aqueous Solutions at 5, 25, and 45°C. I. Apparent Molal Volumes, Bulletin of chemical society of Japan, Vol.48, No.3 (1975): 783-787
7. Peter I Nagy, 'Competing Intramolecular vs. Intermolecular Hydrogen Bonds in Solution', Int J Mol Sci. volume 15(11) (2014): 19562–19633.
8. Soriano-Correa C et al. Theoretical study of the competition between intramolecular hydrogen bonds and solvation in the Cys-Asn-Ser tripeptide. J Phys Chem B. volume 114(27) (2010) :8961-70.
9. Herschlag D, Pinney MM., Hydrogen Bonds: Simple after All?, Biochemistry. 2014 Jun 19;57(24):3338-3352.
10. Arunan E., Desiraju G. R., Klein R. A. et al. 'Definition of the hydrogen bond', Pure Appl. Chem. Volume 83 (2011):1637–1641.
11. Grabowski S. J. Theoretical studies of strong hydrogen bonds. Annu. Rep. Prog. Chem. Volume 102 (2006):131–165.
12. Bader R. F. W. Atoms in Molecules: A Quantum Theory. Oxford University Press; New York, NY, USA: 1990.
13. Popelier P. L. A. Atoms in Molecules: An Introduction. Prentice Hall; Harlow, UK: 1999.
14. Koch U., Popelier P. L. A., 'Characterization of C–H–O hydrogen bonds on the basis of the charge density'. J. Phys. Chem. Volume 99 (1995):9747–9754.
15. Klein R.A. Ab initio conformational studies on diols and binary diol-water systems using DFT methods. Intramolecular hydrogen bonding and 1:1 complex formation with water. J. Comput. Chem. Volume 23 (2002):585–599.
16. Mandado M., Grana A.M., Mosquera R.A., 'Do 1,2-ethanediol and 1,2-dihydroxybenzene present intramolecular hydrogen bond?' Phys. Chem. Chem. Phys. Volume 6 (2004):4391–4396.

