Acoustical, Thermophysical and Excess Properties of Binary and Higher Order Multicomponent Liquid Mixtures

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Abstract: ***Thermophysical, thermoacoustical, non-linearity parameter, available volume and intermolecular free length have been computed for four binary, one ternary and one quaternary systems at 298.15 K. Molar compressibility, specific acoustic impedance and molar sound velocity have also been computed from experimentally determined values of ultrasonic velocity and density. Further, excess internal pressure and excess Gibbs free energy of activation of viscous flow values have been employed to predict the interactions for all the six systems to get a better understanding for the intermolecular interactions taking place thereof.***

Keywords: Multi-component, excess, interactions, thermophysical, thermoacoustical

1.Introduction

An increasing interest in the study of intermolecular interactions coupled with an ever soaring demand for the predictive equations especially for the higher order liquid mixtures forms the basis of the present investigation. Thermodynamic, transport, and thermophysical properties in conjunction with thermoacoustical parameters are the most significant parameters needed to understand the physicochemical characteristics of a system leading to interpretation of the molecular interactions taking place thereof. Knowledge of these properties pave the way for critical information relating to process design and equipments.

Over the years, internal pressure has proven to be an important tool for the study of intermolecular interactions in binary and multi-component liquid mixtures and used as a vital tool to study internal structure, clustering phenomenon and ordered structure [1-4]. Internal pressure of liquid and liquid mixtures can be computed from the experimental values of thermal expansion coefficient, α, and isothermal compressibility, β_T. This approach has been used extensively to study internal pressure, cohesive energy density and energy of vaporization of pure liquids, binary liquid mixtures and solutions [1, 5-9].

Thermoacoustical parameters have been employed successfully to explain intermolecular interactions in liquids over past several years [10- 15]. It is possible to obtain information relating to internal pressure, clustering, inter-molecular spacing etc. from the values of non-linearity parameter, B/A, which plays a significant role in non-linear acoustics[16-20] ranging from under water acoustics to medicine. Four methods, viz., two thermoacoustical, Hartmann Balizer and Ballou[13], have been used for the computation of the non-linearity parameter.

Available volume[12,13,21], V_a, and intermolecular free-length (L_f) [13,22,23] two very important parameters are often used to study the extent of intermolecular interactions in liquids and liquid mixtures[12,13,21]. Number of theoretical approaches have been proposed for estimating the B/A, available volume and intermolecular free length [13,23,24] for pure liquids and liquid mixtures . Ultrasonic velocity and density [22,25-30]has been adequately employed to compute aforementioned parameters in understanding the molecular interactions in pure, binary, and higher order multi-component liquid mixtures. The present investigation work is an extension of our earlier investigations involving comparative studies of ultrasonic velocity [31] and viscosity[32] on the same systems.

The excess parameters have also been computed viz., excess internal pressure(P_i^E) and excess Gibbs free energy of activation(ΔG^{*E}) of viscous flow. The experimental values for the present investigation have been taken from literature [4]. All the earlier mentioned thermodynamic, thermophysical, thermoacoustical, non-linearity parameter(B/A), available volume, intermolecular free length and the interaction parameters have been computed for the following at 298.15 K for:

2.Four Binary Systems

cyclohexane (1) + benzene(2)
n-hexane(1) + cyclohexane(2)
n-hexane(1) + benzene(2)
n-decane(1) + cyclohexane (2)

One ternary: n-hexane(1) + cyclohexane (2) + benzene (3)
One quaternary: n-decane (1) + n-hexane (2) + cyclohexane(3) + benzene(4)
over the entire mole fraction range.

3.Theoretical

Internal pressure has been computed with the help of the equation:

$$(P_{\text{int}})_{mix} = \left(\frac{\alpha_{mix} T_{mix}}{\kappa_{Tmix}}\right) \qquad (1)$$

For the binary, ternary and the quaternary liquid mixture, under investigation, where α_{mix} and κ_{Tmix} represent coefficient of thermal expansion and isothermal compressibility of the binary and higher order liquid mixtures respectively and have been computed by methods given elsewhere[13] .

The energy of vaporization [4,5] is evaluated by the expression

$$\Delta E_{Vap(mix)} = \left(\frac{\alpha_{mix} T}{\kappa_{Tmix}}\right)V = P_{\text{int}(mix)} \mathrm{V} \qquad (2)$$

Where V is the molar volume and all the other symbols have their usual meaning.

The cohesive energy density (CED) [5] is given by

$$CED = n\frac{(\Delta \mathrm{Evap})}{V} \qquad (3)$$

Where n approaches unity for non- polar liquids.

The aforementioned parameter has been employed for correlation of the solubility parameter as

$$\delta = \sqrt{\mathrm{CED}} \qquad (4)$$

In order to calculate heat of vaporization[5] following equation has been used which involved energy of vaporization and is given by

$$\Delta H_{vap} = \Delta E_{vap} + RT \qquad (5)$$

Where all the symbols have their usual meaning.

Coefficient of thermal expansion was used for computing all the thermoacoustical parameters[13], viz., Moelwyn Hughes parameter(C1) , Sharma parameter(S*), isochoric temperature coefficient(X), isobaric and isochoric acoustical parameters (K and K”) and isothermal acoustical parameter(K’)

Available volume [12] has been computed by two methods viz. ultrasonic and thermoacoustical.

$$V_{a(ultrasonic\ )} = V_m\left(1 - \frac{u}{u_\infty}\right) \qquad (6)$$

Where u is the ultrasonic velocity at temperature T and u_∞ is 1600 ms^{-1}. V_m is the molar volume.

$$V_{a(thermoacoustical\ )} = \frac{V_m}{K'+1} \qquad (7)$$

In order to extend the utility of Gruneisen parameter for structural studies of liquids, its pseudo counterpart is defined as

$$\Gamma = \frac{\alpha u^2}{C_p} \qquad (8)$$

Where u is the ultrasonic velocity, and C_p, the heat capacity at constant pressure. Suitable rearrangement gives

$$\Gamma = \frac{\gamma - 1}{\alpha T} \qquad (9)$$

Where γ is specific heat ratio. In the present investigation, computation of non-linearity parameter has been done by calculating pseudo Gruneisen [4] parameter(not reported) and used .

For computing the non-linearity parameter, B/A, the isothermal compressibility, β_T has been computed by an approach given elsewhere[13,21].

The expression for B/A is given by,

$$B/A = 2\mathrm{K} + 2\gamma_{\mathrm{i}}\mathrm{K}'' \qquad (10)$$

$$\left(\frac{B}{A}\right)_{thermoacoustical\ \ (i)} = 2\mathrm{K} + 2\gamma_{\mathrm{i}}\mathrm{K}'' \qquad (11)$$

Where $\gamma_{\mathrm{i}} = \frac{\beta_T}{\beta_s}$, the isothermal compressibility is computed from literature [5]

and

$$\left(\frac{B}{A}\right)_{thermoacoustical\ \ (ii)} = 2\mathrm{K} + 2\gamma_{\mathrm{ii}}\mathrm{K}'' \qquad (12)$$

Where

$\gamma_{\mathrm{ii}} = \alpha T\Gamma + 1$

Hartmann and Balizer [13] obtained the following relation for B/A:

$$\left(\frac{B}{A}\right) = 2 + \left(\frac{0.98 \text{ X } 10^4}{\mathrm{u}}\right), \text{ where u is in ms}^{-1}. \qquad (13)$$

Empirical relation proposed by Ballou[13] is given

$$\left(\frac{B}{A}\right) = -0.5 + \left(\frac{1.2 \text{ X } 10^4}{\mathrm{u}}\right) \qquad (14)$$

Furthermore, ultrasonic velocity and density were used to compute various parameters like Intermolecular free-length (L_f) [21,22], adiabatic compressibility (β_S), molar sound velocity (R), molar compressibility and specific acoustic impedance (Z) [22,27-30].

$$\text{Intermolecular Free length: } \mathrm{L_f} = K\beta_s{}^{1/2} \qquad (15)$$

Where β_S is the adiabatic compressibility given by:

$$\beta_s = \frac{1}{u^2\rho} \qquad (16)$$

$$\text{And Jacobson Constant: } K = (93.875 + 0.375T)10^{-8} \qquad (17)$$

$$\text{Molar sound velocity: } R = u^{1/3}V_m \qquad (18)$$

$$\text{Specific Acoustic Impedance: } \mathrm{Z} = \rho u \qquad (19)$$

$$\text{Molar Compressibility:} \mathrm{B} = \left(\frac{M}{\rho}\right)\beta_s{}^{-1/7} \qquad (20)$$

Where all the symbols have their usual meaning.

The excess internal pressure, $(P_{\text{int}})^E$ is given by

$$P_{\text{int}}{}^{E} = (P_{\text{int}})_{mix} - P_{\text{int}}{}^{id} = (P_{\text{int}})_{mix} - \sum (P_{\text{int}})_i . \phi_i \qquad (21)$$

The excess Gibbs energy of activation of viscous flow[33] has been calculated by making use of the following equation:

$$\Delta G^{*E} = RT[\ln(\eta V)_{mix} - \sum x_i \ln(\eta_i V_i).] \qquad (22)$$

Where η and V represent the viscosity molar volume of the mixtures and the pure components.

4.Results and Discussions

Density (ρ), ultrasonic velocity (u), coefficient of thermal expansion (α), isothermal compressibility (β_T) and viscosity (η) values of the pure components comprising the various binary, ternary and the quaternary liquid mixtures are taken from literature [4] and recorded in Table 1. The computed values of the thermophysical parameters, viz., internal pressure, solubility parameter, energy of vaporization and enthalpy of vaporization for the liquid mixtures have been plotted [Figs. 1a- 1d] against the mole fraction of the first component, x_1, for the four binary systems. The values of the aforementioned parameters for the ternary and the quaternary systems are recorded in Table 2. The variation non-linearity parameter, B/A, vs. the mole fraction of the first component, x_1, are shown for the binary, and higher order multi-component mixtures in Figures 3(a-d). Intermolecular free length, molar compressibility, specific acoustic impedance (Z) and molar sound velocity (R) have been plotted [Fig. 2] for the four binaries. For the ternary and the quaternary liquid mixtures, these values are recorded in Table 2. Excess internal pressure and excess Gibbs energy of activation for viscous flow values are tabulated in Table 3(binary) and Fig 4(ternary and quaternary) for the systems chosen for the present investigation at 298.15 K.

5.Binary Systems

Fig. 1a clearly reveals that the internal pressure values for system1, cyclohexane (x_1) + benzene (x_2), are highest amongst all the four binaries and the values are seen to decrease with the increase in the mole fraction of the first component. This trend is seen to be replicated in all the four binary systems. System 2, n-hexane(x_1) + cyclohexane (x_2) exhibit the largest decrease with increase in x_1. These results are seen to be in agreement with the literature data [4] for all the binary systems under investigation. The excess internal pressure (P_i^E) values are found to be negative for all the binary systems and are in good accordance with the literature values [4].

Figs. 1(b-d) exhibit the variation of solubility parameter, energy of vaporization and enthalpy of vaporization respectively with the mole fraction of the first component for the four binary systems under investigation. The figures show that the values of the aforementioned parameters indicate an increasing trend for the systems 1, 3 and 4 viz., cyclohexane (x_1) + benzene(x_2), n-hexane(x_1) + benzene(x_2) and n-decane(x_1) + cyclohexane (x_2) respectively whereas system 2, n-hexane(x_1) + cyclohexane(x_2) does not exhibit any such trend for all the three parameters with values being more or less consistent over the entire mole fraction range. This behavior is seen to be most pronounced for system 4 for the all the parameters under consideration. This may be attributed to the internal pressure for system 4 which shows the least decreasing trend (Fig. 1a) amongst all the four binary systems taken for the study.

The available volume (not reported) computed by the ultrasonic (Eq. 6) approach and by the thermoacoustical approach (Eq. 7) follows an increasing trend with the increase in mole fraction of the first component for all the four binary systems at 298.15 K. Figs. 3a-d show the variation of non-linearity parameter (B/A) computed by four different approaches viz., Balizer (Eq. 13), Ballou (Eq. 14), thermoacoustical (i) and (ii), with x_1. The trend exhibited by all the four approaches is found to be similar in all the six systems. Balizer approach shows the maximum value of B/A while the thermoacoustical (i) route gives the lowest value. Another interesting thing to be noted is that the B/A values computed by thermoacoustical route (ii) are on the higher side than those computed by (i). This may be attributed to the contribution coming from the pseudo Gruneisen parameter. A look at Fig.2 (a) shows that the intermolecular free length values tend to increase with the increase in x_1 for all the four binary systems. These findings seem to be in agreement with the reported values of ultrasonic velocity in literature [4] which indicate a decrease with increasing mole fraction of the first component. The value of Jacobson's constant does not show any variation as it is a temperature dependent constant. This also explains the decreasing trend of Z (Fig. 2c) for all the systems under consideration. Both molar compressibility, B (Fig. 2b), and Molar sound velocity, R (Fig. 2d), show an increase with the increase in the mole fraction of the first component.

Multi-component liquid Mixtures

Ternary system: n-hexane (x_1) + cyclohexane (x_2) + Benzene(x_3)
Quaternary system: n-decane (x_1) + n-hexane(x_2) + cyclohexane(x_3) + Benzene(x_4)
A perusal of table 2 shows that the values of internal pressure, P_i, do not follow a specific trend with the increase in the mole fraction of the first component (x_1). This may be attributed to the irregularity in the values of ultrasonic velocity and density [5], for both the ternary and the quaternary systems, which affects the value of internal pressure accordingly. The values of solubility parameter, energy of vaporization and enthalpy of vaporization do not show much variation and remain consistent over the entire composition range. The thermoacoustical parameters show a similar trend as exhibited by that in the binary systems.

Tables 2 further show that the intermolecular free length values exhibit an increasing trend with the increase in x_1 for both ternary and the quaternary systems. Both molar compressibility (B) and Molar sound velocity (R) show an increase in the values with the increase in the mole fraction of the first component. There is a decreasing trend in the value of specific acoustic impedance, Z, for both the systems under consideration. Overall, the trends are similar to that seen in the binary systems. The non-linearity parameter, B/A, for the ternary system (Fig.3c) follows a similar trend as shown by the binary systems with the highest B/A values being shown by the Balizer (Eq.13) approach and the least values being given by the thermoacoustical approach(i) when plotted against the mole fraction of the first component . A similar trend is also observed for the values of the non-linearity parameter computed by the four different approaches for the quaternary system (Fig. 3d) too.

Excess Properties

A perusal of excess internal pressure values (Table 3) for the first two systems,viz., cyclohexane (x_1) + benzene (x_2) and n-hexane (x_1) + cyclohexane (x_2) respectively, shows that the values are on the lower side for the first system. On the whole , the values are found to be the highest for the system comprising of n-hexane(x_1) + benzene(x_2) while the least are given by the system comprising of n-decane(x_1) + cyclohexane (x_2) with the remaining two systems lying in between. From earlier studies it can be surmised that the higher negative values of excess internal pressure indicate stronger interaction between the components comprising the system. Thus we might infer that in the cyclohexane rich region for the systems, cyclohexane (x_1) + benzene (x_2) and n-hexane (x_1) + cyclohexane (x_2), the interactions are comparatively weaker (Table 3). On comparing n-hexane(x_1)+ cyclohexane(x_2) with n-hexane(x_1)+benzene(x_2) , we find that replacement of cyclohexane with benzene keeping n-hexane as the common hydrocarbon in both the systems, results in an increased degree of interaction resulting in the highest values of excess internal pressure (negative) amongst all the four binary systems. Another interesting observation is that the highest (negative) values of excess internal pressure and seen to be present in the benzene rich regions for the two binary systems containing benzene as one of the components. The difference in the values of the excess internal pressure may be attributed to vicinity of approach of the two very unlike molecules having significantly different molecular sizes.

These results seem to be in good agreement with earlier results [34] of related excess parameters, namely, excess isothermal compressibility, β_S^E, values. The binary systems consisting of cylohexane + n-alkane, viz., n-hexane and n-decane show a decrease in the excess values of internal pressure with increase in carbon number while going from n-hexane to n-decane. These results are also seen to be in good agreement with earlier results [34-36]. Further, it is seen that as the mole fraction of n-hexane is increased for both the systems, interactions become stronger which is justified by the higher negative values from Table 3.

The ΔG^{*E} values in Table 3 clearly indicate that they are positive for the binary system consisting of n-decane+ cyclohexane whereas negative for all the other three binary systems, thereby indicating a much lower degree of interaction occurring in this system than the other three binary systems. This is further validated by the lowest values of excess internal pressure. The highest (negative) values are given by the system comprising of n-hexane + benzene indicating greater interaction between the components, a finding also supported by the excess internal pressure values.

The P_i^E values of the ternary system recorded in Fig.4 show that they are negative over the entire range of composition. A closer look further reveals that the excess values are higher in all those cases where the benzene mole fraction lies in the vicinity of 0.5. This indicates that the interactions are on the higher side in the benzene rich regions. For the quaternary system (Fig. 4) we find that in the decane scarce region, with mole factions, x_1 less than 0.1275, the excess values are on the higher side. Increase in the decane concentration lowers the excess values indicating towards decrease in the extent of interaction. The ΔG^{*E} values for the ternary and quaternary system in Fig. 4 indicates that the values are negative. It is a well-known fact that negative values of excess functions indicate strong interactions hinting at formation of intermolecular complexes and positive values are pointer towards weak interactions.

6. Conclusion

The observed findings stem from the fact that n-hexane has a higher amount of disorder [36] than n-decane which is more ordered. Introduction of a second component results in creation of an additional free volume in case of the higher alkane due to partial breaking of order For the two binary systems 2 and 4, which consist of cyclohexane as a common hydrocarbon, as the chain length of the normal hydrocarbon increases from 6 to 10, the interactions tend to decrease.
P_i^E values for the system cyclohexane (x_1) + benzene (x_2) are found to be lesser than for n-hexane (x_1) + cyclohexane (x_2). This is probably due to the fact that both cyclohexane and benzene are planar and very stable, hence the interactions between them is less as compared to the interactions between n-hexane and cyclohexane. A closer inspection of these two systems reveal that the excess internal pressure starts reducing as the mole fraction of cyclohexane is increased since the interactions become weaker. The difference in the values of the excess internal pressure may be attributed to vicinity of approach of the two very unlike molecules having significantly different molecular sizes. Nature and extent of molecular interactions are usually expressed in terms of excess functions. Since these interactions play a very vital role in getting an in-depth knowledge of the complete scenario of a system, one pathway to achieve this goal is to study the thermophysical, thermoacoustical and non-linearity parameter in conjunction with some excess parameters to get a better understanding of the various intermolecular interactions taking place thereof.

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References

[1] Marcus Y., Chem. Rev. 2013; 113:6536-6551.
[2] Praharaj M.K., Satapathy A, Mishra P, Mishra S., Theoretical & App. Phys. 2013;7:23.
[3] Santhi N., Sabarathinam P., Alamelumangai G., Madhumitha J., Emayavaramban M. , Int.Lett. Chem. Phys. and Astronomy. 2012, 5:1-7.
[4] Shukla R.K., Shukla S.K., Pandey V.K., Awasthi P., J.Mol Liq. 2008;137:104-109.
[5] Dey R, Saini A, Sharma A.K., PandeyJ. D., J. Mol. Liq. 2014; 195:195-196.
[6] Dey R, Singh A.K., Pandey J.D., J. Mol. Liq. 2006; 124:121-123.
[7] Pandey J. D.,Shukla S.K., Chhabra J and Dey R., J. Indian Chem. Soc. 2004;81:962-964.
[8] HildebrandJ.H.,Scott R. L., Reinhold. New York. 1964.
[9] Dack M R J., J. Chem. Soc. Rev., 1975; 4:211-219.
[10] Dubey G.P., Sharma M., Oswal S., J.Chem. Thermodynamics 2009;41:849–858.
[11] Zorebski E., Goralski P., Godula B., Zorebski M., J. Chem. Thermodynamics 2014, 68:145–152.
[12] Pandey J.D., Dey R., Bhatt B.D., *PhysChemComm*. 2002; 5:37-39.
[13] Dey R., Kumar P., *Acta Acustica*. 2011; 97:8-13.
[14] Pandey J.D.,Dubey G.D., Dey R, Dubey S.N., ActaAcustica.1997;83:90-92.
[15] Tabhane V.A., Ghosh S, Agarwal S., J. Pure Appl. Ultrason. 1999; 21:122-126.
[16] Cain C.A., Nishiyama H., Katakura K., J. Acoust. Soc. Amer. 1986; 80:685-688.
[17] Endo H. J.,,Acoust. Soc. Amer. 1988; 83: 2043 - 2046.
[18] Jie T., Dong Yanwu and Zhao Hegyuan, Kexue Tongbao.1988;33:1511.
[19] Jugan J, Abdulkhadar M., J. Mol. Liq. 2002; 100:212-227.
[20] Dey R, Singh A.K, Soni N.K, Bish B.S, Pandey J.D., Pramana-J.Phys. 2005; 67:389-394.
[21] Pandey J.D., Dey R. Chabbra J., PhysChemComm.2003; 6:55-58.

[22] Pandey P.K., Awasthi A, Awasthi A. ,Phy. Chem. Liq.2013; 52:.416-427.
[23] Pandey J.D., Dey R, Upadhayaya M., Acoust. Lett. 1997; 21:120-125.
[24] Rathnam M.V., Bhanushali K.R., Sayed R.T., Kumar M.S.S., J. Mol. Liq. 2012;173:35-41.
[25] López AB, Abuín A.G, Díaz D G, La Rubia M.D., Navaza J.M., J. Chem. Thermodynamics 2013;61:1-6.
[26] Papari M.M., Ghodrati H, Fadaei F, Sadeghi R, Behrouz S, Soltani Rad M.N. Moghadasi J., J. Mol. Liq. 2013;180:121-128.
[27] Pandey P.K., Awasthi A, Awasthi A. ,Phys. Chem. Liq. 2014; 52:320-330.
[28] Awasthi A, Rastogi M, Shukla J.P., Fluid Phase Equilibria. 2004; 215:119-127.
[29] Rastogi M, Awasthi A, Gupta M, Shukla J.P., J Mol Liq. 2003;107:185-204.
[30] Awasthi A, Shukla J.P., Ultrasonics, 2003;41:477-486.
[31] Dey, R, Harshavardhan A., J. Energy ChemEngg. 2014; 2:1-7.
[32] Dey, R, Harshavardhan A., Springer Book Series ,In press (2014).
[33] Dubey G.P, Kumar Krishan, J. Chem. Thermodynamics, 2012;50:7-14.
[34] Dominiguez M, Pardo J., Santafe J., Royo F.M, Urieta J S., Fluid Phase Equil,1996; 118: 227-240.
[35] Aicart E., Tardajos G., Diaz Pena M. J. Chem. Engg. Data, 1980;25:140-145.
[36] Junquera E.,Tardajos G. Aicart E., J. Chem. Thermodynamics,1988;20:1461-1467.

Table 1. Ultrasonic velocity, density and other parameters of the pure components at 298.15 K. [Ref. 4]

Compound	Molecular wt (g/mol)	Molar volume (cm^3/mol)	Density (Kg/m^3)	Ultrasonic velocity (m/s)	α x 10^3 (K^{-1})	β_T x 10^{12} (m^2N^{-1})	P_i (MPa)
Cyclohexane	84.16	108.82	773.3	1252.0	1.2150	114.00	414.49
Benzene	78.11	89.45	873.1	1296.0	1.2264	87.70	393.59
n-Hexane	86.18	131.53	655.2	1076.0	1.3897	160.60	223.30
n- Decane	142.29	195.94	726.2	1225.0	1.0500	116.20	209.88

Table 3. Range of excess internal pressure (P_i^E) and excess Gibbs (ΔG^{*E}) energy of activation of viscous flow at 298.15 K.

S. No.	System	Excess internal pressure (MPa)		Excess Gibbs energy of activation of viscous flow (KJ/mol)	
		Maximum	Minimum	Maximum	Minimum
1	cyclohexane (x_1) + benzene (x_2)	-58.82 (x_1- 0.2609)	-33.93 (x_1- 0.7128)	-0.48 (x_1-0.4887)	-0.29 (x_1-0.7128)
2	n- hexane (x_1) + cyclohexane (x_2)	-61.31 (x_1- 0.6702)	-19.69 (x_1-0.0684)	-0.47 (x_1-0.5903)	-0.09 (x_1-0.0684)
3	n-hexane (x_1) + benzene (x_2)	-73.17 (x_1 -0.1599)	-63.83 (x_1-0.7811)	-0.57 (x_1-0.5070)	-0.35 (x_1-0.1599)
4	n-decane (x_1) + cyclohexane (x_2)	-11.95 (x_1-0.1357)	-4.37 (x_1=0.2677)	0.08 (x_1-0.1357)	0.02 (x_1-0.3563)

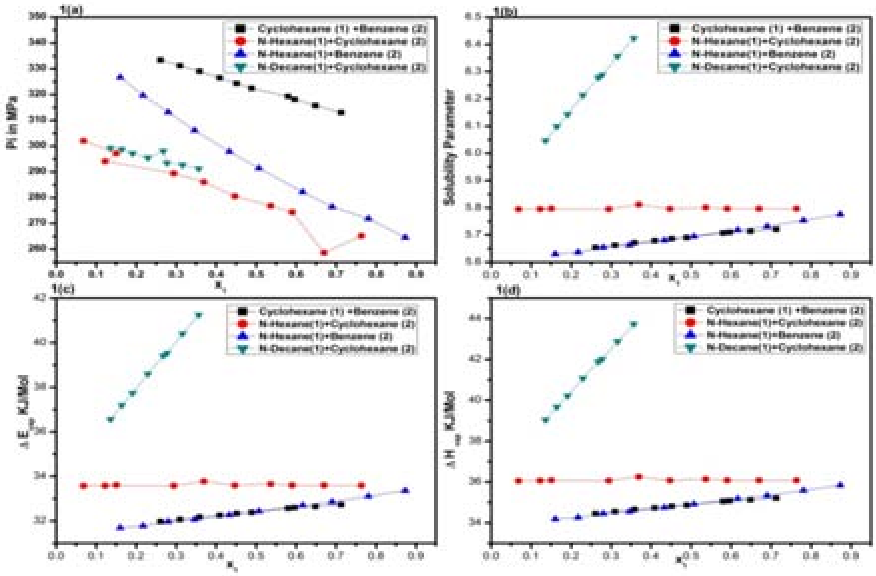

Figure 1: Plots of Pi, solubility, ΔE_{vap}, ΔH_{vap} Vs x_1 for binary systems

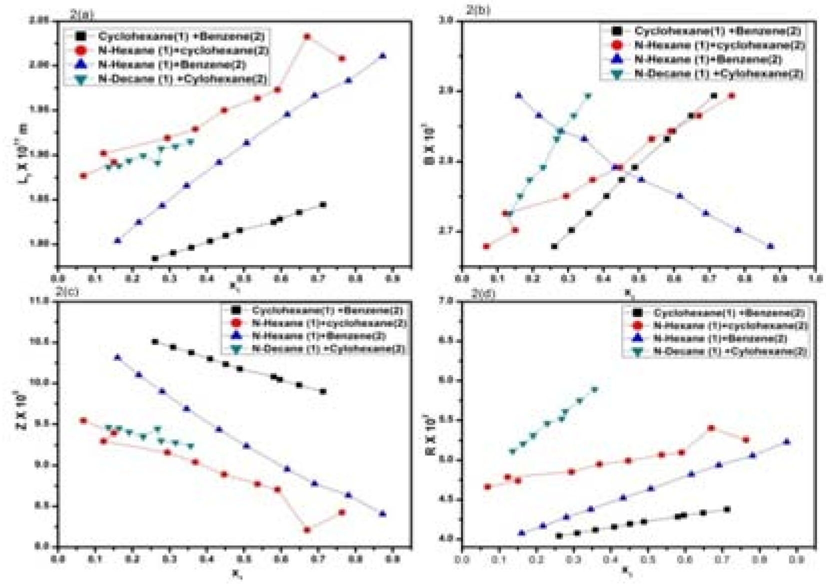

Figure 2: Plots of Lf, B, Z & R Vs x_1 for binary systems

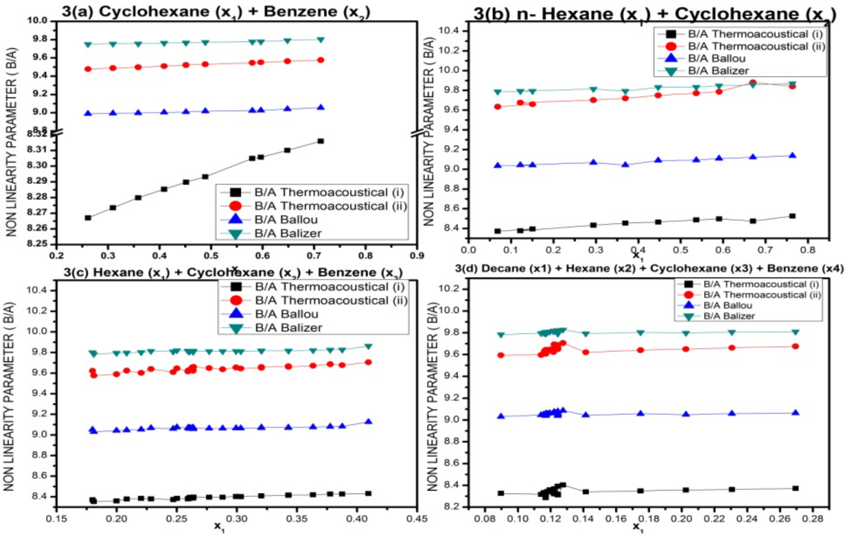

Figure 3: Plots of B/A Vs x_1 for binary, ternary & quaternary systems.

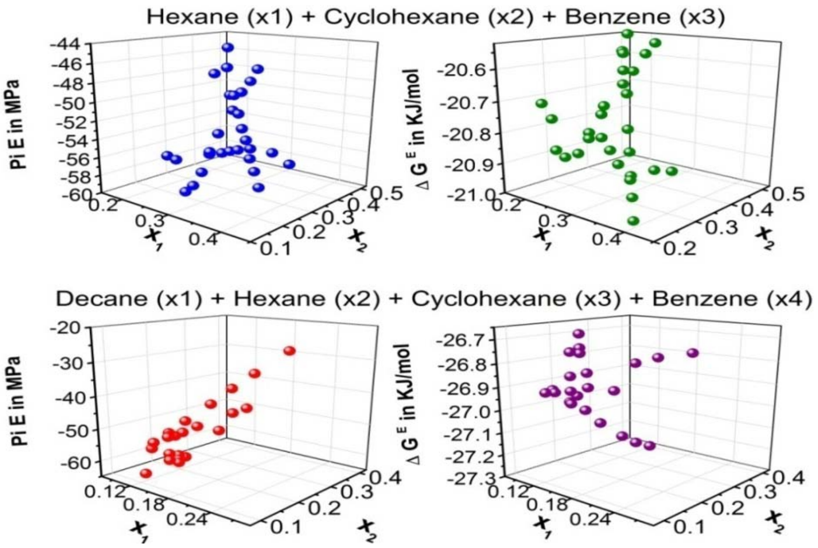

Figure 4: Plots of Pi^E, ΔG^E Vs x_1 for ternary & quaternary systems.

Table 2: Thermophysical, thermoacoustical, non-linearity parameter (L_f), molar compressibility (B), Specific acoustic impedance (Z), Molar sound velocity (R) for the ternary and quaternary system at 298.15K.

n-hexane(x_1) + cyclohexane (x_2) + benzene (x_3)									
x_1	x_2	P_i (Mpa)	δ x 10^{-2} (kJ $m^{-3})^{1/2}$	ΔE_{vap} (kJ/ mol)	ΔH_{vap} (kJ/ mol)	L_fx10^{11} (m)	Bx10^3 (m^3 mol^{-1}) $(kg^{-1}ms^2)^{-1/7}$	ZX 5-Oct (kg m^{-2} s^{-1})	RX10^2 (m^3 mol^{-1}) $(ms^{-1})^{1/3}$
0.1799	0.4805	304.4	5.72	32.76	35.24	1.87	2.97	9.63	4.51
0.181	0.2625	313.2	5.69	32.35	34.83	1.84	2.86	9.89	4.34
0.1998	0.2649	310.7	5.69	32.35	34.83	1.85	2.88	9.82	4.36
0.2083	0.4311	304	5.72	32.76	35.24	1.87	2.97	9.61	4.52
0.2204	0.3673	308.3	5.71	32.61	35.09	1.86	2.92	9.75	4.43
0.2286	0.4086	301.1	5.72	32.67	35.15	1.88	2.99	9.53	4.54
0.247	0.2256	306.6	5.69	32.32	34.8	1.86	2.91	9.7	4.41
0.2501	0.3826	299.9	5.71	32.64	35.11	1.89	2.99	9.49	4.55
0.2605	0.2855	303.5	5.7	32.48	34.96	1.87	2.95	9.6	4.48
0.2607	0.3149	302.8	5.71	32.58	35.06	1.88	2.96	9.58	4.5
0.2611	0.3686	301.9	5.72	32.66	35.14	1.88	2.98	9.56	4.52
0.2629	0.4249	298	5.73	32.81	35.29	1.89	3.03	9.43	4.6
0.2639	0.4499	297.1	5.73	32.88	35.36	1.89	3.04	9.4	4.63
0.2769	0.3583	299.4	5.72	32.72	35.2	1.89	3.01	9.47	4.57
0.3032	0.2849	300.1	5.71	32.62	35.1	1.88	2.99	9.49	4.55
0.3203	0.3107	297.3	5.72	32.69	35.17	1.89	3.02	9.41	4.59
0.3428	0.2847	295.8	5.72	32.71	35.19	1.9	3.04	9.36	4.62
0.3634	0.2634	294.8	5.72	32.7	35.18	1.9	3.04	9.33	4.63
0.3776	0.2978	292.4	5.73	32.81	35.28	1.91	3.07	9.26	4.68
0.3876	0.2356	293.9	5.72	32.68	35.16	1.91	3.05	9.31	4.64
0.4095	0.2962	288.7	5.72	32.67	35.15	1.92	3.09	9.17	4.7

n-decane(x_1) + n-hexane(x_2) + cyclohexane (x_3) + benzene (x_4)										
x_1	**x_2**	**x_3**	**P_i (Mpa)**	**δ x 10^{-2} (kJ $m^{-3})^{1/2}$**	**ΔE_{vap} (kJ/mol)**	**ΔH_{vap} (kJ/mol)**	**L_fx 10^{11}(m)**	**Bx10^3 (m^3mol^{-1}) $(kg^{-1}$ $ms^2)^{-1/7}$**	**Z X10^{-5} (kg $m^{-2}s^{-1}$)**	**R X10^2 (m^3 mol^{-1})$(ms^{-1})^{1/3}$**
0.09	0.173	0.186	309.6	5.868	34.43	36.91	1.85	3.07	9.78	4.67
0.114	0.143	0.188	309.4	5.907	34.89	37.37	1.86	3.12	9.78	4.73
0.116	0.177	0.329	302	5.948	35.38	37.86	1.88	3.23	9.55	4.91
0.117	0.117	0.277	303.2	5.919	35.04	37.51	1.87	3.18	9.59	4.84
0.117	0.177	0.188	306.3	5.916	35	37.48	1.86	3.15	9.69	4.78
0.118	0.211	0.192	302.7	5.929	35.15	37.63	1.88	3.2	9.58	4.86
0.12	0.248	0.195	299.8	5.94	35.28	37.76	1.89	3.24	9.48	4.92
0.122	0.21	0.384	295.9	5.969	35.62	38.1	1.9	3.3	9.37	5.03
0.124	0.344	0.204	291.9	5.97	35.64	38.12	1.91	3.34	9.24	5.1
0.128	0.383	0.208	288.6	5.985	35.82	38.3	1.92	3.39	9.14	5.18
0.142	0.181	0.195	304.5	5.978	35.74	38.22	1.87	3.24	9.62	4.92
0.175	0.191	0.205	300.8	6.047	36.57	39.05	1.88	3.35	9.51	5.09
0.203	0.195	0.211	298.9	6.111	37.35	39.82	1.89	3.44	9.45	5.23
0.231	0.199	0.215	296.7	6.167	38.03	40.51	1.89	3.52	9.39	5.36
0.269	0.207	0.221	294.2	6.247	39.03	41.5	1.9	3.64	9.31	5.55