Internal pressure, excess internal pressure and pseudo-Gruneisen parameter of binary systems from associated and non-associated models

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Density and speed of sound have been measured earlier for binary liquid mixtures formed by formamide, N-methylacetamide, di-methylformamide and di-methylacetamide with acetonitrile at 293.15, 298.15, 303.15, 308.15 and 313.15 K and atmospheric pressure over the whole concentration range. Pseudo-Gruneisen parameter and internal pressure have been derived from the measured values of density and ultrasonic velocity. These values are compared with the theoretical values obtained by the utilization of Flory theory, Ramaswamy and Anbananthan model and model suggested by Glinski to predict the behaviour of weakly interacting liquids. The observed properties derived from measured data are fitted to Redlich-Kister polynomial relation to estimate the binary coefficients and standard errors. Excess internal pressure parameter for these binary mixtures is also computed to study the molecular interactions involved in the liquid systems.

Keywords: Pseudo-Gruneisen parameter, Internal pressure, Flory theory, Ramaswamy and Anbananthan model, Redlich-Kister

The role of internal pressure in liquid solution thermodynamics was recognized by Hildebrand. The use of this property for a long time was qualitative but recently its usefulness has been explored for quantitative study of intermolecular forces. Pioneer attempts have been made by several workers to study the significance and its correlation with other properties. A liquid under a small isothermal volume expansion does work against the cohesive force which causes the change in the internal energy (E). The function \( (\partial E/\partial V)_{T} \) is called internal pressure. Hildebrand showed that for non-polar liquids, \( (\partial E/\partial V)_{T} = n \Delta E_{vap}/V \), where \( \Delta E_{vap} \) represents the energy of vaporization of the liquid and V its molar volume. The quantity n approaches energy density. For polar liquids n ranges from 0.32-1.624. Internal pressure and cohesive energy density (c.e.d.), evidently, do not reflect the same physical property of these liquids. Our one of the aim is to analyze the physical significance of internal pressure and cohesive energy density and to demonstrate the usefulness of both properties.

Two liquids do not completely mix if one liquid has much greater cohesion than the other. Conversely, molecules in liquids of similar cohesion are just as likely to interact and mix with each other as with their own kind. Any interaction between unlike molecules enhances the change of miscibility. Hildebrand has referred to the square root of c.e.d. as the solubility parameter because of its frequent use in solubility problems. The internal pressure of liquid mixtures were computed from the knowledge of thermal expansion coefficient (\( \alpha \)) and isothermal compressibility (\( \beta_{T} \)).

The internal pressure can be computed by indirect methods as suggested by Suryanarayan. In recent past, substantial amount of work has been carried out by many workers to study the excess thermodynamic functions like excess internal pressure; excess energy of vaporization, excess pseudo-Gruneisen parameter and is still in progress.

Gruneisen parameter is an important tool to study the thermodynamic and other properties of solid crystalline lattice. The concept of anharmonicity of the lattice is characterized by the Gruneisen parameter. 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 Gruneisen parameter can also be used to study them. Its pseudo counterpart has been found to be suitable to investigate the internal structures, clustering phenomenon and other quasi crystalline properties of liquids including liquid mixtures\textsuperscript{15-18}, liquefied gases\textsuperscript{19}, liquid metal alloys\textsuperscript{20} and higher alkanes\textsuperscript{15}.

In the present investigation, internal pressure, excess internal pressure and Pseudo-Gruneisen parameter were derived from the measured values of density and ultrasonic velocity\textsuperscript{21} for binary liquid mixtures formed by formamide, N-methylacetamide (NMA), di-methylformamide (DMF) and di-methylacetamide (DMA) with acetonitrile at 293.15, 298.15, 303.15, 308.15 and 313.15 K and atmospheric pressure over the whole concentration range. A comparison of experimental and theoretical speed of sound is provided in Table 1. These derived values of internal pressure were compared with the theoretical values obtained by the utilization of Flory theory\textsuperscript{22,23}, Ramaswamy and Anbananthan model\textsuperscript{24} and model suggested by Glinski\textsuperscript{25} to predict the behavior of weakly interacting liquids. The observed properties derived from measured data were fitted to Redlich-Kister polynomial relation\textsuperscript{26} to estimate the binary coefficients and standard errors.

### Computational methods

#### Flory theory

Assuming two body interactions, Flory evaluated the reduced and characteristic parameters of the liquid mixture from the reduced equation of state derived from the resulting partition function as:

\[ \frac{P}{\tilde{V}} = \frac{V^{1/3}}{T} - \frac{1}{VT} \]

where, \( \tilde{P} = \frac{P}{P^*} \), \( \tilde{T} = \frac{T}{T^*} \), and \( \tilde{V} = \frac{V}{V^*} \)

where \( P, T, V \) are reduced parameters and \( P^*, T^*, V^* \) are characteristic parameters. The coefficient of thermal expansion, \( \alpha \), is evaluated from the reduced equation of state as:

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \alpha \times 10^3 ) K</th>
<th>( \beta_T \times 10^{12} ) Pa</th>
<th>V/cm\textsuperscript{3}mole\textsuperscript{-1}</th>
<th>T</th>
<th>( \rho_{exp}/g.cm^{-3} )</th>
<th>( \rho^*_w/g.cm^{-3} )</th>
<th>( u_{exp}/ms^{-1} )</th>
<th>( U^*_w/ms^{-1} )</th>
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* Ref.30
\[
\alpha_{Flory} = \frac{1}{T} \left[ \frac{1}{3 (V - 1) - 1} \right] \quad \text{...(2)}
\]

and adiabatic compressibility, \( \beta_s \) is given by,
\[
\beta_s = \frac{1}{u^2 \rho} \quad \text{...(3)}
\]

where, \( u \) and \( \rho \) are speed of sound and density of binary liquid mixture. By combining above equations Pseudo-Greneisen parameter for liquid mixtures is obtained as;
\[
\tau_{Flory} = \frac{1}{T} \left[ \frac{1}{\beta_s} - \gamma_p - \frac{1}{\alpha} \right] \quad \text{...(4)}
\]

where \( \gamma_p \) is the thermal pressure coefficient and related to the following expression as;
\[
\gamma_p = \frac{P^T}{TV} \quad \text{...(5)}
\]

\( \gamma_p \) is also related to internal pressure of the liquid mixture as;
\[
P_{Flory} = T \gamma_p \quad \text{...(6)}
\]

For observed value of Pseudo-Gruneisen parameter, \( \gamma_p \) is evaluated by the relation as;
\[
\gamma_p = \frac{\alpha}{\beta_T} \quad \text{...(7)}
\]

Thermal expansion coefficient, \( \alpha \) and adiabatic compressibility, \( \beta_T \) are defined as;
\[
\alpha = (0.0191 \times \beta_T)^{1/4} \quad \text{...(8)}
\]
\[
\beta_T = 1.71 \times 10^{-3} / T^{4/3} \times u^2 \times p^{4/5} \quad \text{...(9)}
\]

**Ramsamy and Anbananthan Model**

Ramsamy and Anbananthan\(^{24}\) proposed the model based on the assumption of linearity of acoustic impedance with the mole fraction of components. Further it is assumed, that an equilibrium physical property such as viscosity, refractive index, surface tension etc which are based on linearity can also be predicted. Glinski\(^{25}\) assumed that when solute is added to solvent the molecules interact according to the equilibrium,
\[
A + B \leftrightarrow AB \quad \text{...(10)}
\]

and the association constant, \( K_{as} \), can be defined as;
\[
K_{as} = \frac{[AB]}{[A][B]} \quad \text{...(11)}
\]

where \([A]\) is amount of solvent and \([B]\) is amount of solute in the liquid mixture. By applying the condition of linearity with composition, internal pressure can be obtained as;
\[
P_{i_{cal}} = x_A P_{i_A} + x_{AB} P_{iAB} \quad \text{...(12)}
\]

where \( x_A \), \( x_{AB}P_{iA} \) and \( P_{iAB} \) and \( P_{i_{cal}} \) are the mole fraction of A, mole fraction of associate AB, internal pressure of A, internal pressure of associate AB and calculated internal pressure respectively. The associate AB cannot be obtained in its pure form. Following simplifications have been made in Eq. (12), firstly, molar concentration term should be replaced by activities for concentrated solution and second, the equilibrium reaction is not complete by definition; i.e. there are also molecules of non-associated component present in the liquid mixture even prevailing in the high solute content. The Eq. (12) takes the form,
\[
P_{i_{cal}} = [x_A P_{iA} + x_B P_{iB} + x_{AB} P_{iAB}] \quad \text{...(13)}
\]

The general idea of this model can be, however, exploited as;
\[
K_{as} = \frac{\Sigma (Pi_{obs} - Pi_{cal})^2}{\Sigma (Pi_{obs} - Pi_{obs})} \quad \text{...(16)}
\]

where \( C_A \) and \( C_B \) are initial molar concentrations of the components. One can take any value of association constant, \( K_{as} \), and calculate the equilibrium value of \([AB]\) for every composition of the mixture. Replacing molar concentration by equi-molar activities for concentrated solution, Eq. (14) becomes,
\[
K_{as} = \frac{a_{AB}}{a_A - a_{AB}} \quad \text{...(15)}
\]

where \( a_A \), \( a_{AB} \) and \( a_{AB} \) are the activity of component A, Component B and associate, AB respectively.

Similarly, assuming any value of internal pressure for hypothetical pure component AB, the internal pressure of liquid mixture, \( P_{i_{cal}} \) can be calculated by substituting the value of association constant. Now, it is possible to compare the internal pressure calculated using Eq (14) with the experimental values. On changing both the adjustable parameters \( K_{as} \) and \( P_{iAB} \) gradually, one can get different values of the sum of squares of deviations,
The minimum value of $S$ can be obtained theoretically by a pair of the fitted parameters. But we found that for some $K_{as}$ and $P_{iAB}$, the value of $S$ is high and changes rapidly, and for others, it is low and changes slowly when changing the fitted parameters. The condition which is prevailing in the process of adjustment is that the value of $P_{iAB}$ should not be much lower than the lowest $P_{oAB}$ of the system or much higher than the highest one. Quantitatively, it should be reasonable to accept the pair of adjustable parameters $K_{as}$ and $P_{iAB}$ which has the physical sense and which reproduces the experimental physical property satisfactorily.

On inspecting the results obtained from Ramaswamy and Anbananthan model, Glisnki$^{25}$ suggested the equation assuming additivity with the volume fraction, $\phi$ of the components, the refined version of Natta and Baccaredda model$^{27}$ as,

$$P_{i_{cal}} = \frac{P_i A P_i B P_i AB}{\phi_A P_i A P_i AB + \phi_B P_i A P_i AB + \phi AB P_i A P_i B}$$

...(17)

where $P_{i_{cal}}$ is the theoretical internal pressure of binary liquid mixture, $\phi_A$, $\phi_B$ are the volume fractions of component A and B and $P_{iA}$, $P_{iB}$ and $P_{iAB}$ are the internal of components A, B and AB. The numerical procedure and determination of association constant, $K_{as}$, were similar to that described before and the advantage of this method as compared with the earlier one was that the data on densities of liquid mixture are not necessary except those of pure components needed to calculate the volume fractions.

**Results and Discussion**

Relations between association phenomena in liquids were analyzed earlier$^{28}$ by considering van der Waals equation of state which was based only on simple averaged geometrical deviations without analyzing the system in terms of equilibrium. The association phenomenon has been related usually the deviation of different quantities from additivity. Ramaswami and Anbananthan derived the model based on the assumption of linearity of acoustic impedance with the mole fraction of components which was corrected$^{25}$ and tested$^{28}$ to predict the associational behaviour. The quantities analyzed were refractive index, molar volume, viscosity, intermolecular free length. Prediction of internal pressure and pseudo-Gruneisen parameter from this approach is our first attempt. The results of fittings obtained from the model were utilized properly. The basic doubt regarding this model except the assumption of linearity of internal pressure and pseudo-Gruneisen parameter with mole fraction is that these liquids have poor affinity to form dimmers. The calculations were performed using a computer program which allows fittings easily both the adjustable parameters simultaneously or the parameters were changed manually.

We constructed the data sheet in a computer program with association constant $K_{as}$ and $P_{iAB}$ as the fitted parameters. $P_{iAB}$ is the internal pressure in the pure component AB; i.e. a hypothetical liquid having only the associate AB. On changing these parameters, the equilibrium concentrations of species [A], [B] and [AB] will change and the internal pressure pseudo-Gruneisen parameter can be computed. The difference between observed and theoretical values for internal pressure and pseudo-Gruneisen parameter is used to obtain the sum of squares of deviation. It is assumed that in solution three associates instead of two are formed (A, B and AB). The values of internal pressure and pseudo-Gruneisen parameter in pure associate can be treated as a fitted one with the value of $K_{as}$.

The standard deviation $\Delta Pi$ can be represented mathematically by Redlich-Kister polynomial equation$^{26}$ for correlating the experimental data as;

$$y = x_i (1 - x_i) \sum_{i=0}^{p} A_i (2x_i - 1)^i$$

...(18)

where $y$ refers to deviation in internal pressure $y$, $\Delta Pi$. $x_i$ is the mole fraction and $A_i$ is the coefficient. The values of coefficients were determined by a multiple regression analysis based on the least square method and are summarized along with the standard deviations between the experimental and fitted values of the respective function in Table 2. The standard deviation is defined by,

$$\delta = \left[ \frac{\sum_{i=1}^{m} (y_{exp} - y_{cal})^2}{(m-p)} \right]^{1/2}$$

...(19)

where $m$ is the number of experimental points and $p$ is the number of adjustable parameters. The values of standard deviations lie between 0.0047 – 0.03723 TP a respectively.

The absolute average percent deviations (AAPD) in internal pressure, excess internal pressure and pseudo-Gruneisen parameter obtained from different models are provided in Table 3 whereas mixture data are presented in Table 4. A careful full perusal of Tables 3 and 4 indicate
Table 2 — Coefficients of the redlich-kister equation and standard deviations (\(\delta\)) for internal pressure of binary liquid mixtures at various temperatures.

<table>
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<tr>
<th>Acetonitrile+Formamide</th>
<th>T</th>
<th>(A_0/\text{TPa})</th>
<th>(A_1/\text{TPa})</th>
<th>(A_2/\text{TPa})</th>
<th>(A_3/\text{TPa})</th>
<th>(\delta/\text{TPa})</th>
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Table 3 — Comparison of absolute average percent deviation (AAPD) values obtained from various liquid state mode Acetonitrile+Formamide

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<th>(K_{ac})</th>
<th>(\tau_{Flory})</th>
<th>(\tau_{RS})</th>
<th>(\tau_{GLI})</th>
<th>(\Pi_{Flory/\text{TPa}})</th>
<th>(\Pi_{RS/\text{TPa}})</th>
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Acetonitrile+NMA

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Acetonitrile+DMF

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Table 4 — Experimental density (ρ), experimental ultrasonic velocity (u_{exp}), observed pseudo gruniesen parameter (τ_{obs}), observed internal pressure (P_{obs}), and theoretical values of pseudo gruniesen parameter and internal pressure obtained from various models for binary liquid mixtures at various temperatures.

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(Contd.)
Table 4 — Experimental density ($\rho_{\text{exp}}$), experimental ultrasonic velocity ($u_{\text{exp}}$), observed pseudo grueneisen parameter ($\tau_{\text{obs}}$), observed internal pressure ($P_{\text{obs}}$), and theoretical values of pseudo grueneisen parameter and internal pressure obtained from various models for binary liquid mixtures at various temperatures. (Contd.)

| $x_1$ | $\rho_{\text{exp}} / g\cdot cm^{-3}$ | $u_{\text{exp}} / m\cdot s^{-1}$ | $P_{\text{obs}} / 9\text{ Pa}$ | $P_{\text{theo}} / 10^3\text{ Pa}$ | $P_{\text{exp}} / 10^6\text{ Pa}$ | $P_{\tau_{\text{obs}}} / \tau_{\text{obs}}$ | $x_1$ | $\rho_{\text{exp}} / g\cdot cm^{-3}$ | $u_{\text{exp}} / m\cdot s^{-1}$ | $P_{\text{obs}} / 9\text{ Pa}$ | $P_{\text{theo}} / 10^3\text{ Pa}$ | $P_{\text{exp}} / 10^6\text{ Pa}$ | $P_{\tau_{\text{obs}}} / \tau_{\text{obs}}$ |
|-------|-----------------------------------|---------------------------------|-------------------------------|-------------------|-------------------|-------------------|-------|-----------------------------------|---------------------------------|-------------------------------|-------------------|-------------------|-------------------|-------------------|
| 0.8340 | 0.8405                            | 1300.8                          | 3.704                         | 3.693             | 3.641             | 4.757             | 0.8340 | 0.8405                            | 1300.8                          | 3.704                         | 3.693             | 3.641             | 4.757             | 0.8340 |
| 0.9187 | 0.7992                            | 1260.8                          | 3.367                         | 3.497             | 3.354             | 4.595             | 0.9187 | 0.7992                            | 1260.8                          | 3.367                         | 3.497             | 3.354             | 4.595             | 0.9187 |

Acetonitrile + DMF

293.15

| 0.2142 | 0.9391                            | 1470.2                          | 4.666                         | 4.522             | 4.523             | 4.557             | 0.2142 | 0.9391                            | 1470.2                          | 4.666                         | 4.522             | 4.523             | 4.557             | 0.2142 |

Acetonitrile + DMA

298.15

| 0.9075 | 0.8253                            | 1356.7                          | 3.652                         | 3.584             | 3.510             | 3.527             | 0.9075 | 0.8253                            | 1356.7                          | 3.652                         | 3.584             | 3.510             | 3.527             | 0.9075 |

303.15

| 0.9567 | 0.7899                            | 1301.9                          | 3.267                         | 3.471             | 3.251             | 3.259             | 0.9567 | 0.7899                            | 1301.9                          | 3.267                         | 3.471             | 3.251             | 3.259             | 0.9567 |

308.15

| 0.2142 | 0.9304                            | 1452.8                          | 4.550                         | 4.569             | 4.417             | 4.450             | 0.2142 | 0.9304                            | 1452.8                          | 4.550                         | 4.569             | 4.417             | 4.450             | 0.2142 |

313.15

| 0.9075 | 0.8234                            | 1311.0                          | 3.581                         | 3.483             | 3.392             | 3.399             | 0.9075 | 0.8234                            | 1311.0                          | 3.581                         | 3.483             | 3.392             | 3.399             | 0.9075 |

318.15

| 0.9567 | 0.7853                            | 1299.1                          | 3.330                         | 3.422             | 3.225             | 3.233             | 0.9567 | 0.7853                            | 1299.1                          | 3.330                         | 3.422             | 3.225             | 3.233             | 0.9567 |

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Exp/RS

$\tau_{\text{obs}}$

$\rho_{\text{exp}}$

$u_{\text{exp}}$

$P_{\text{obs}}$

$P_{\text{theo}}$

$P_{\text{exp}}$

$P_{\tau_{\text{obs}}}$
that associated processes provide fairly good results as compared to non-associated. Higher deviation values in Flory model can be explained as the model was developed for non-electrolyte \( \gamma \)-meric spherical chain molecules and the system under investigation have interacting and associating properties. Moreover, the expression used for the computation of \( \alpha \) and \( \beta^T \) are also empirical in nature. Table 4 indicates that with the increase of mole fraction, the values of density, theoretical pseudo-Gruneisen parameters and theoretical internal pressure obtained from all the models decrease at all temperatures.

Excess internal pressure can be defined as:

\[
P^{E} = P_{mix} - P_{idl}
\]

and

\[
P_{idl} = x_1 P_1 + x_2 P_2
\]

where \( P^{E} \) is the excess internal pressure, \( P_{idl} \) is the ideal internal pressure and \( P_{mix} \) is internal pressure of liquid mixture respectively.

Variation of excess internal pressure, \( P^{E} \), with composition at various temperatures is presented in Figs 1-4. For excess properties, sign and magnitude are of much important to describe the molecular

---

Fig. 1 — Plot of excess internal pressure \( P^{E} \), with mole fraction \( x_1 \) for \( x \) acetonitrile + \((1-x)\) formamide; ♦, excess internal pressure from PFP model; ■, excess internal pressure RS model; ▲, excess internal pressure from Glinski model.

Fig. 2 — Plot of excess internal pressure \( P^{E} \), with mole fraction \( x_1 \) for \( x \) acetonitrile + \((1-x)\) NMA; ♦, excess internal pressure from PFP model; ■, excess internal pressure RS model; ▲, excess internal pressure from Glinski model.

Fig. 3 — Plot of excess internal pressure \( P^{E} \), with mole fraction \( x_1 \) for \( x \) acetonitrile + \((1-x)\) DMF; ♦, excess internal pressure from PFP model; ■, excess internal pressure RS model; ▲, excess internal pressure from Glinski model.
interactions involved in the liquid system. A careful look in all the figures indicates that no regular trends are observed for excess internal pressure. Negative values of $P_i^E$ show the strong molecular interactions between the liquid components. Dispersion type interactions and structural effects arising from interstitial accommodation because of differences in molecular volumes and free volumes between liquid components contribute negative terms to $P_i^E$. The repulsive forces between the loan pair of electrons leads to positive values of $P_i^E$ suggest the presence of weak interactions between the component molecules and the favoring packing of unlike molecules.

Conclusion
Conclusively, models assuming associated processes give more reliable results as compared to non-associated processes and helpful in deducing the internal structure of associates through the fitted values of pseudo-Gruneisen parameter and internal pressure in a hypothetical pure associate and observed dependence of concentration on composition of a mixture.

Acknowledgement
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References