5.1 Introduction

The non-linearity parameter B/A plays a significant role in non-linear acoustics and its determination is of increasing interest in a number of areas ranging from underwater acoustics to medicine. B/A of liquids can be obtained from the variation of sound velocity with temperature and pressure. A number of experimental and theoretical studies have been performed on the non-linearity parameter of liquids making use of phenomenological [1-3] or thermodynamic methods [4,5]. Also some studies on B/A have been performed from the viewpoint of theory of liquids [6]. B/A values for organic liquids [2,3,7] liquid mixtures [6,8,9] and biological samples [10,11] have been reported. Tong et al. [12] calculated the B/A values for pure liquids making use of Schaaff's equation [13] for sound velocity. Although detailed studies of the non-linearity parameter have been made for many pure liquids, such studies are sparse in the case of liquid mixtures.

This chapter (Chapter 5) deals with the theoretical calculation of the non-linearity parameter B/A of five binary liquid mixtures of nitrobenzene, chlorobenzene,
bromobenzene, toluene, benzene and methyl ethyl ketone (MEK) with methyl ethyl ketone as a common component, making use of ultrasonic velocity at two temperatures and at atmospheric pressure. The ultrasonic velocity, density, adiabatic compressibility and molecular radius required for the present calculations are taken from the literature [14,15], even though the ultrasonic velocities in these binary liquid mixtures were measured in the present study. We made use of the Tong and Dong equation [12] for pure liquids and Flory’s statistical theory [16,17] for calculating B/A values. The thermodynamical parameters in Tong’s equation were calculated for binary mixtures using Flory’s theory. The variations of B/A with mole fractions of MEK are discussed. Also similar to other thermodynamical parameter we define an excess non-linearity parameter [18] \((B/A)^E\) for liquid mixtures. The binary liquid systems chosen for the present study are

1. Methyl Ethyl Ketone (MEK) + Nitrobenzene
2. Methyl Ethyl Ketone (MEK) + Chlorobenzene
3. Methyl Ethyl Ketone (MEK) + Bromobenzene
4. Methyl Ethyl Ketone (MEK) + Toluene
5. Methyl Ethyl Ketone (MEK) + Benzene

5.2 Theory

Finite amplitude waves travel non-linearly in fluids. This non-linearity can be described by the equation of state \(p = p(\rho, s)\), where \(p\) the pressure, \(\rho\) the density and \(s\) the entropy of the liquid. Expansion of this equation in a Taylor series for the isentropic case give
Expressing the expansion with two temperature dependent coefficients \( A \) and \( B \) as follows:

\[
p = p_0 + A \left( \frac{\rho - \rho_0}{\rho_0} \right) + B \left( \frac{\rho - \rho_0}{\rho_0} \right)^2 + \ldots \quad \text{--------- (5.2)}
\]

The temperature depending coefficients \( A \) and \( B \) are given by

\[
A = \rho_0 \left( \frac{\partial p}{\partial \rho} \right)_{s, \rho = \rho_0} \quad \text{--------- (5.3)}
\]

\[
B = \rho_0^2 \left( \frac{\partial^2 p}{\partial \rho^2} \right)_{s, \rho = \rho_0} \quad \text{--------- (5.4)}
\]

The ratio \( B/A \) which is a significant quantity in non-linear acoustics is referred to as acoustics non-linearity parameter \( B/A \). Beyer [17] simplified the equation for \( B/A \) using thermodynamical transformations as

\[
B/A = 2\rho_0 C_0 \left( \frac{\partial C}{\partial p} \right)_{s, \rho = \rho_0} \quad \text{--------- (5.5)}
\]

where \( C_0 \) is the sound velocity at equilibrium.

Replacing \( C_0^2 = \left( \frac{\partial p}{\partial \rho} \right)_{s, \rho = \rho_0} \) equation 5.5 can be modified as [12]

\[
B/A = \rho_0 \left( \frac{\partial C_0^2}{\partial p} \right)_{s, \rho = \rho_0} \quad \text{--------- (5.6)}
\]

In the following deduction, omit the subscript ‘0’, but all variables will take the value at equilibrium.
Tong et al. [12] applied Schaaff's [13] equation for sound velocity in equation 5.7 and obtained the equation for B/A as

\[
B/A = \rho \left( \frac{\partial C^2}{\partial p} \right)
\]

\[\text{------------------------ (5.7)}\]

\[
B/A = J(0) + J(X)
\]

\[\text{------------------------ (5.8)}\]

where

\[
J(0) = \left(1 - \frac{1}{\gamma}\right)\frac{C^2 \rho K_T}{T\beta}
\]

\[\text{------------------------ (5.9)}\]

and

\[
J(X) = \frac{2(3-2X)^2}{3(X-1)(6-5X)}
\]

\[\text{------------------------ (5.10)}\]

where \( \gamma \) is the ratio of specific heat, \( \rho \) is the density, \( K_T \) is the isothermal compressibility, \( T \) is the temperature, \( \beta \) is the expansibility and \( X \) is the real volume of a mole of molecule. \( X \) is the ratio of molecular weight to the product to \( \rho b \), where \( b \) is the Van der Waal’s constant given by \( b = \frac{16}{3} \pi \frac{r_0^3 N_A}{b} \), \( r_0 \) being the molecular radius and \( N_A \) is the Avogadro number.

In the present study the thermodynamical parameter containing in equations (5.9) and (5.10) which are required to calculate B/A values of binary mixtures are obtained as follows.

Starting from the reduced equation of state from Flory’s statistical theory [16,17]

\[
\frac{PV}{T} = \frac{V}{\gamma^{\frac{1}{2}}} - \frac{1}{\gamma^{\frac{1}{2}}} - V\gamma
\]

\[\text{------------------------ (5.11)}\]

where

\[
\tilde{V} = V/V^*
\]

\[\text{------------------------ (5.12)}\]

\[
\tilde{T} = T/T^*
\]

\[\text{------------------------ (5.13)}\]
In the above equations (5.1) to (5.15) $P$, $V$, $T$ are pressure, volume and temperature, $\tilde{P}, \tilde{V}, \tilde{T}$ are reduced pressure, reduced volume and reduced temperature and $P^*, V^*, T^*$ are characteristic pressure, characteristic volume and characteristic temperature respectively. Using equations 5.12 to 5.15 determine the characteristic and reduced parameters for pure liquids.

The effective molecular weight $\bar{M}$ and volume $V_{12}$ are given by

$$\bar{M} = x_1M_1 + x_2M_2 \quad \text{------------------- (5.16)}$$

$$V_{12} = \frac{\bar{M}}{\rho_{12}} \quad \text{------------------- (5.17)}$$

where $y_1$, $y_2$ are the mole fractions and $M_1$ and $M_2$ are respectively the molecular weights of first and second pure liquids. $\rho_{12}$ is the density of the liquid mixture.

Flory’s characteristic and reduced parameters for binary mixtures were calculated by the method adopted by Panday [20,21] is as follows,

The reduced volume of the mixture is obtained as

$$\tilde{V} = \phi_1 \tilde{V}_1 + \phi_2 \tilde{V}_2 + \left\{V_E/ \left( x_1V^*_1 + x_2V^*_2 \right) \right\} \quad \text{------------------- (5.18)}$$

where $V^E$ is the molar excess volume of the liquid mixture given by

$$V^E = V_{12} - x_1V_1 - x_2V_2 \quad \text{------------------- (5.19)}$$
and the segment fraction $\phi_i$ is given by

$$\phi_i = x_i V^*_i / \left( x_1 V^*_1 + x_2 V^*_2 \right)$$  \hspace{1cm} (5.20)

t = 2 for binary mixtures

$T^*, P^*$ and $V^*$ for the mixture are calculated as

$$T^* = T V^* / \left( \frac{\gamma - 1}{V - 1} \right)$$  \hspace{1cm} (5.21)

$$P^* = T \left\{ \frac{\phi_1 P^*_1}{T^*_1} + \frac{\phi_2 P^*_2}{T^*_2} \right\}$$  \hspace{1cm} (5.22)

and $V^* = x_1 V^*_1 + x_2 V^*_2$  \hspace{1cm} (5.23)

The thermodynamical parameters necessary to calculate B/A values for binary mixture are obtained by the following relations derived by Khanwalkar [22]

$$\beta = \frac{3 \left( \frac{\gamma - 1}{V - 1} \right)}{T \left[ 1 - 3 \left( \frac{\gamma}{V - 1} \right) \right]}$$  \hspace{1cm} (5.24)

$$C_p = \tilde{C}_p \left( \frac{P^* V^*}{T^*} \right)$$  \hspace{1cm} (5.25)

where

$$\tilde{C}_p = \frac{C_p^E + x_1 C_{p1} + x_2 C_{p2}}{\left( \frac{P^* V^*}{T^*} \right)}$$  \hspace{1cm} (5.26)

$$C_p^E = \frac{P^* V^*}{T^*} \left[ \frac{1}{3 \left( \frac{\gamma}{V - 1} \right)} - \frac{x_1}{\frac{\gamma}{V_1 - 1}} - \frac{x_2}{\frac{\gamma}{V_2 - 1}} \right]$$  \hspace{1cm} (5.27)

$$K_r = K_s + \frac{TV_{12} \beta^2}{C_p}$$  \hspace{1cm} (5.28)

where $K_s$ is the adiabatic compressibility of the mixture
Van der Waal’s constant $b$ and real volume of a mole of molecule $X$ for binary liquid mixtures are calculated as

$$b = x_1b_1 + x_2b_2 \quad \text{------------------- (5.30)}$$

$$X = \frac{x_1M_1 + x_2M_2}{\rho_vb} \quad \text{------------------- (5.31)}$$

The excess properties of the mixtures are defined as the difference between the thermodynamic functions of mixing for a real solution in excess to those for an ideal solution. In studying liquid mixtures, excess properties are more important than thermodynamical properties [23]. Similar to excess thermodynamic functions for binary liquid mixtures, an excess non linearity parameter $(B/A)^E$ for binary mixtures is defined [18].

$$(B/A)^E = (B/A)_{\text{mix}} - (B/A)_{\text{id}} \quad \text{------------------- (5.32)}$$

where $(B/A)_{\text{mix}}$ is the theoretically calculated values and $(B/A)_{\text{id}}$ is that obtained from ideal components defined as

$$(B/A)_{\text{id}} = x_1(B/A)_1 - x_2(B/A)_2 \quad \text{------------------- (5.33)}$$

The sound velocity, density, adiabatic compressibility and molecular radius required for the present calculations are taken from the literature [14,15].

5.3 Results and Discussions

Acoustic non-linearity parameter $B/A$ calculated for five binary mixtures at two different temperatures are given in table 5.1. The table also contains $B/A$ of pure liquids.
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**MEK + Benzene**

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**MEK + Toluene**

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**MEK + Chlorobenzene**

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It is found that B/A values decrease as the mole fractions of MEK increases. The B/A for liquids has been interpreted as the quantity representing the magnitude of hardness of the liquid [6], which may be considered to be true for the liquid mixtures as well. For all the five binary mixtures, as the mole fraction of MEK increase the density and ultrasonic velocity decrease and hence compressibility increases. Therefore as the mole fraction of MEK increases the bulk modulus, hence B/A must decrease.

The Plots of excess isentropic compressibility and excess (B/A), (B/A) are shown figures 5.1 and 5.2.

![Figure 5.1 Excess compressibility vs mole fraction of MEK at 30°C](image)

**Figure 5.1** Excess compressibility vs mole fraction of MEK at 30°C
It is interesting to note that \((B/A)^E\) values are all negative and show the same trend as that of the excess isentropic compressibility. A negative compressibility is an indication of strong interaction in liquid mixtures [24] which has been attributed to charge transfer, dipole induced dipole, and dipole-dipole interactions while a positive sign indicating weak interaction has been interpreted as due to dispersion force [25].

The detailed explanation of molecular interactions existing in the present binary liquid mixtures was discussed in Section 3.5 of Chapter 3. So a brief description is as follows. In MEK + benzene system there is a dipole interaction between \(\pi\) electrons in the benzene ring and the carbonyl group \(>\text{CO}\) of MEK. Also in MEK + toluene there is a dipole interaction between \(>\text{CO}\) and \(\text{CH}_3\) group of MEK by no bond resonance. In the other mixtures the same type of interaction
are present between >CO and -Cl , -Br or -NO₂ of chlorobenzene, bromobenzene and nitrobenzene. The difference in magnitude of \((B/A)^E\) for different mixtures is attributable to the difference in the extent of interactions present in them.

Out of the present five binary systems with MEK as a common component nitrobenzene has the largest dipole moment and benzene has zero dipole moment. Therefore molecular interaction with MEK is largest for nitrobenzene and least for benzene. This is why nitrobenzene has large negative values of \((B/A)^E\) and benzene has least negative values of \((B/A)^E\). This is in accordance with the study of excess isentropic compressibility values.

5.4 Conclusion

Acoustic non-linearity parameter \(B/A\) is calculated for five binary mixtures with methyl ethyl ketone as a common component at two different temperatures. Similar to excess isentropic compressibility, an excess non-linearity parameter \((B/A)^E\) is defined which shows the same type of variation as that of excess isentropic compressibility. Molecular interaction between unlike molecules are briefly discussed using \((B/A)^E\) values. It is concluded that \((B/A)^E\) is an important quantity similar to other thermodynamic parameters useful for explaining the interaction in binary liquid mixtures.
References