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Non-linearity parameter B/A of binary liquid mixtures at elevated pressures

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Abstract. When sound waves of high amplitude propagate, several non-linear effects occur. Ultrasonic studies in liquid mixtures provide valuable information about structure and interaction in such systems. The present investigation comprises of theoretical evaluation of the acoustic non-linearity parameter B/A of four binary liquid mixtures using Tong and Dong equation at high pressures and $T = 303.15$ K. Thermodynamic method has also been used to calculate the non-linearity parameter after making certain approximations.

Keywords. Non-linearity parameter; binary liquid mixtures; ultrasonic velocity.

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1. Introduction

Most of the parameters involved in ultrasonic studies have been deduced by considering the propagation of acoustic waves of infinitesimal amplitude. But when sound waves of high amplitude propagate, non-linear effects occur such as harmonic distortion and acoustic scattering. It has become of much interest to predict the extent of various kinds of non-linear effects in acoustics [1–4]. It is possible to obtain certain information about internal pressures, clustering, inter-molecular spacing etc., from the values of the non-linearity parameter, which plays a significant role in non-linear acoustics ranging from underwater acoustics to medicine. A number of experimental and theoretical investigations have been carried out on the non-linearity parameter of liquids. Tong and Dong [5] determined B/A for pure liquids making use of the Schaaff's [6] equation for sound velocity. Non-linearity parameter of binary as well as multicomponent liquid mixtures has also been computed by several workers [7–10]. Recently non-linearity parameter of higher alkanes was computed by Verma *et al* [11].

To the best of our knowledge, computation of B/A on varying pressures has not been carried out. In the present investigation an attempt in this field has been made and B/A is calculated for four binary liquid mixtures at $T = 303.15$ K over a wide range of pressure (ranging from 0.1 to 80 Mpa). In this context, Tong and Dong equation has been used to calculate the B/A values. Scarcity of experimental data and its variation with temperature has hampered workers in this field to evaluate B/A from the more direct thermodynamic

method. Here an attempt has thus been made to compute B/A from the thermodynamic equation by making use of some approximations for evaluating $\mathrm{d}u/\mathrm{d}T$. The results obtained are found to be fairly satisfactory taking into account the approximations used.

Furthermore, a comparative study of B/A values obtained from the two methods has also been carried out, and merits and demerits of both the methods are discussed in the light of molecular structure and intermolecular interactions.

2. Theory

Since sound propagation is an adiabatic process, the non-linearity parameter is to be obtained from the adiabatic equation of state:

$$P = P_0 + A\left[\frac{\rho-\rho_0}{\rho_0}\right] + B/2\left[\frac{\rho-\rho_0}{\rho_0}\right]^2 + \cdots, \tag{1}$$

where

$$A = \rho_0\left[\frac{\partial p}{\partial \rho}\right]_{s,0} = \rho_0 u_0^2,$$

$$B = \rho_0^2\left[\frac{\partial^2 P}{\partial \rho^2}\right]_{s,0} = 2\rho_0^2 u_0^3\left[\frac{\partial u}{\partial P}\right]_{s,0}.$$

Here suffix 0 indicates the equilibrium values and s is entropy. In what follows, suffix 0 is omitted for brevity. The non-linear departure is symbolized by

$$B/A = 2\rho u\left[\frac{\partial u}{\partial P}\right]_s. \tag{2}$$

From eq. (2) the non-linearity parameter is calculated by two different methods, viz., Tong and Dong method and the thermodynamic method. Tong and Dong [5] applied Schaaff's [6] equation for sound velocity, namely;

$$u^2 = \gamma RT\left[\frac{(1/3)M}{(M-\rho b)^2} - \frac{2}{(M-\rho b)}\right] \tag{3}$$

for computing the value of B/A. From eqs (2) and (3), B/A is given by

$$B/A = J(0) + J(x), \tag{4}$$

where

$$J(0) = \left(1-\frac{1}{\gamma}\right)\frac{u^2\rho\beta_T}{\alpha_T},$$

$$J(x) = \frac{2(3-2x)^2}{3(x-1)(6-5x)},$$

with

$$x = M/\rho \cdot b.$$

Here ρ is the density of the mixture, β_T isothermal compressibility, α coefficient of thermal expansion and x is the real volume of molecule. For the present work the values of b_{mix} and x_{mix} for liquid mixtures were obtained from relations

$$x_{\mathrm{mix}} = \sum_{i=1}^{n} y_i M_i / \rho_{\mathrm{mix}} b_{\mathrm{mix}},$$

$$b_{\mathrm{mix}} = \sum_{i=1}^{n} y_i b_i,$$

where y_i is the mole fraction, M_i is the molar mass of ith component and ρ_{mix} is the density of mixture. While computing B/A the isothermal compressibility $\beta_{T(\mathrm{mix})}$ and thermal expansion coefficient α_{mix} have been estimated by using two recently proposed relationships [12]

$$\beta_T(\mathrm{mix}) = \frac{1.71 * 10^{-3}}{T^{4/9} u_{\mathrm{mix}}^2 \rho_{\mathrm{mix}}^{4/3}} \quad \text{and} \quad \frac{\alpha_{\mathrm{mix}}^4}{\beta_T(\mathrm{mix})} = 0.0191, \tag{5}$$

where all the terms have their usual meanings.

In the thermodynamic method the non-linearity parameter B/A of liquids can be obtained from the variation of sound velocity with pressure and temperature. Substituting the relations

$$\left(\frac{\partial u}{\partial P}\right)_s = \left(\frac{\partial u}{\partial P}\right)_T + \left(\frac{\partial T}{\partial P}\right)_s \left(\frac{\partial u}{\partial T}\right)_P,$$

$$\left(\frac{\partial T}{\partial P}\right)_s = (\gamma - 1)(\beta_s/\alpha).$$

B/A can be expressed in the form

$$B/A = 2\rho u \left[\left(\frac{\partial u}{\partial P}\right)_T + (\gamma - 1)\frac{\beta_s}{\alpha}\left(\frac{\partial u}{\partial T}\right)_P\right]. \tag{6}$$

This thermodynamic equation has also been used for estimating B/A.

3. Results and discussion

The values of non-linearity parameter for binary liquid mixtures, viz., toluene + aniline (I), toluene + *o*-xylene (II), benzene + cyclohexane (III), benzene + nitrobenzene (IV) have been represented graphically in the figures from 1 to 4 at various pressures and mole fractions. Takagi and coworkers [13–15] measured experimentally the ultrasonic speeds and densities at 303.15 K and high pressures. The densities were represented in the form of the Tait equation. This data and the Tait equations were taken for computing the various quantities employed in the equation for B/A. Although the non-linearity parameters have

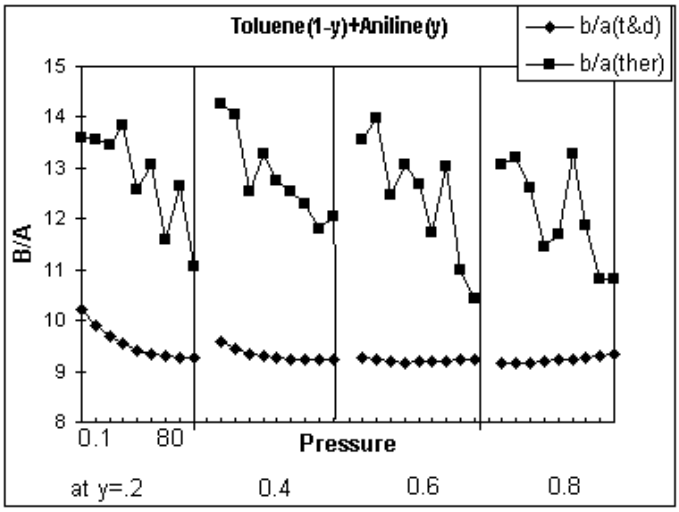

Figure 1. Plot of B/A (Tong and Dong and thermodynamic) vs pressure for toluene + aniline.

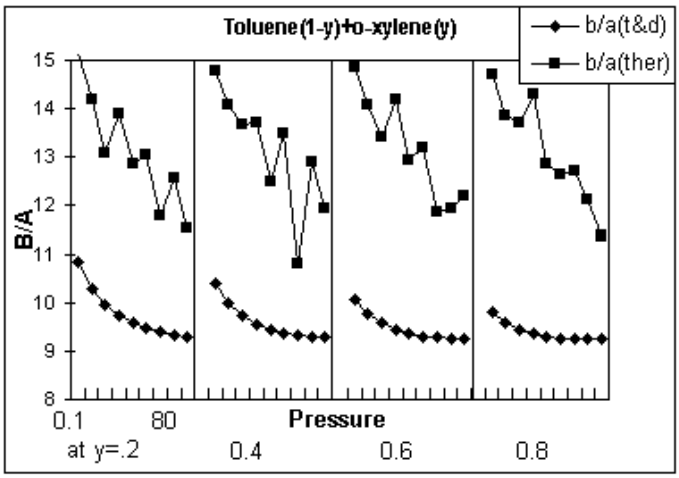

Figure 2. Plot of B/A (Tong and Dong and thermodynamic) vs pressure for toluene + *o*-xylene.

been calculated over a wider range of pressure, scarcity of space has necessitated the tables to be omitted. The complete data can be obtained from the authors on request.

For system (I) toluene + aniline (non-polar + polar), experiments carried out previously [13] show that for binary mixtures including aniline, β_S^E (excess) are negative at atmospheric pressure and change progressively to 0 or positive as the temperature is raised. Furthermore aniline molecule is also known to be associated through H bonding in the pure state and this self-association decreases when it is mixed with some other aromatic

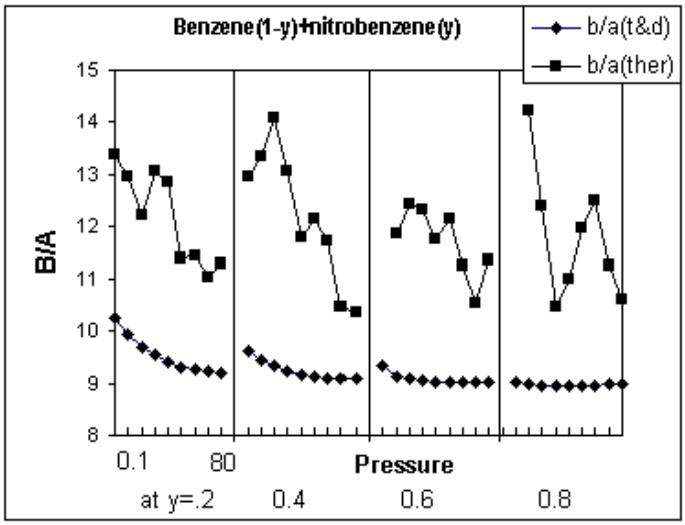

Figure 3. Plot of B/A (Tong and Dong and thermodynamic) vs pressure for benzene + nitrobenzene.

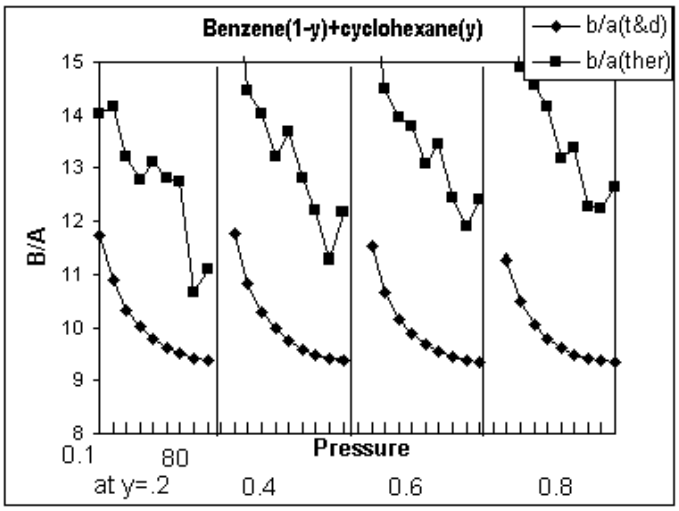

Figure 4. Plot of B/A (Tong and Dong and thermodynamic) vs pressure for benzene + cyclohexane.

compound. Hence we presume that β_S^{E} values would be largely affected by pressure changes since molecular interactions between unlike substances are weak. The values of the non-linearity parameter are found to decrease with increasing pressure at low aniline concentration but in the aniline rich region the non-linearity parameter shows a reverse trend i.e. it increases with increase in pressure.

For the binary liquid mixture toluene + o-xylene (non-polar + non-polar) previously determined values [13] show that β_S^{E} is small and positive at atmospheric pressure and decrease with rise in pressure showing parallel curves. Hence the mixture can be treated in general as regular or ideal as no recognized association takes place between the unlike molecules. In this case the values of the non-linearity parameter from the Tong and Dong equation are again found to decrease with increase in pressure at low o-xylene concentration. As the o-xylene concentration increases, the B/A values still decrease but at high values of pressures some increasing trend is also marked.

Ultrasonic velocity measurements for binary liquid mixture benzene + cyclohexane (non-polar + non-polar) show that ultrasonic speeds increase parabolically with increase in pressure throughout the experimental range. Further, large positive values of excess volumes [14] clearly indicates a nearly linear relation with mole fraction and thus the mixture can generally be treated as approximately ideal. This observation is further strengthened by the fact that B/A values for the aforementioned system calculated by the Tong and Dong equation exhibit the highest values at all the mole fractions as compared to the other binary liquid mixtures under investigation. The values of the non-linearity parameter from the Tong and Dong equation for this liquid mixture show a regular decreasing trend with rise in pressure.

The values of the non-linearity parameter for system (IV) benzene + nitrobenzene (non-polar + polar) decrease as the pressure increases. There is a slight reversal of this trend at high nitrobenzene concentration although it is not so remarkable as in the case of systems containing toluene.

The non-linearity parameter, B/A, calculated by the Tong and Dong equation is made up of two parts (eq. (4)). The $J(0)$ term contributes only 16% of B/A at maximum for all four mixtures mostly due to smaller contribution of the $J(0)$ term to the overall value of B/A. The $J(x)$ term is important which depends upon x the molar volume. The present investigation consists of components having comparative size and nearly spherical or flat shaped structures. Here the flat or planar structure proves to be a major inhibitor for interactions to a very large extent. Another cause which supports to inhibit interactions in the case of benzene is the presence of the de-localized π electron cloud above and below the molecule which gives it extra stability thus preventing a higher degree of interaction. As a result systems containing benzene show a gradual drift towards ideality a fact which is well exhibited by the values of B/A obtained from the Tong and Dong method for the binary liquid mixtures benzene + cyclohexane.

To calculate B/A by the thermodynamic approach, variation of sound velocity with temperature $(\partial u/\partial T)_P$ and pressure $(\partial u/\partial P)_T$ should be known. For the above mentioned binary liquid mixtures, $(\partial u/\partial P)_T$ was directly computed from the data but the variation of ultrasonic velocity with temperature was not available so certain approximations were used.

It was observed that the variation of ultrasonic velocity with density was linear in nature. For all the mixtures ultrasonic velocity was plotted with respect to density, it was found that up to a reasonable extent it was a straight line, i.e.

$$U = A + B\rho. \tag{7}$$

Here A and B are constants depending upon the mixtures studied. Using the definition and the value of the thermal expansion coefficient and taking B as the slope of this line we get

$$du/dT = -B\alpha\rho. \tag{8}$$

Substituting the value of $(\partial u/\partial T)_P$ in the thermodynamic equation, the non-linearity parameter was calculated. The values are found to be on the higher side than from the Tong and Dong equation, as is evident from the graphs but this might be attributed to the approximations involved in the calculations.

A comparative study of the values of B/A calculated by the Tong and Dong equation and the thermodynamic method proposed here, indicates that the thermodynamic approach may prove to be a valuable tool for determination of the non-linearity parameter from the knowledge of the thermal expansion coefficient. Also this method proposed here can be used directly in the absence of the $\mathrm{d}u/\mathrm{d}T$ values.

In the present investigation the four binary liquid mixtures viz. toluene + aniline (non-polar + polar), toluene + *o*-xylene (non-polar + non-polar), benzene + cyclohexane (non-polar + non-polar) and benzene + nitrobenzene (non-polar + polar) have been taken to study all the possible types of intermolecular interactions. Molecular interactions play a key role in understanding the complete picture of the various liquid mixtures taken for the present study and the B/A values of the liquids have been interpreted as the quantity representing the magnitude of the hardness of the liquid. Hence the calculated values prove invaluable in explaining the interactions taking place in the systems taken under consideration.

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