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A comparative study of non-linearity parameter for binary liquid mixtures

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Abstract. The present investigation comprises of theoretical evaluation of acoustic non-linearity parameter, B/A for equimolar binary mixtures, viz. chlorobenzene or 1-chloronaphthalene with a series of normal alkanes (n-C_n, n = 6, 8, 10, 12, 14, 16), and with a series of highly branched alkanes (br-C_n, n = 6, 8, 12, 16), viz. 2,2-dimethylbutane (br-C_6), 2,2,4-trimethylpentane (br-C_8), 2,2,4,6,6-pentamethylheptane (br-C_{12}) and 2,2,4,4,6,8,8-heptamethylnonane (br-C_{16}). Tong and Dong method, thermoacoustical method, Hartmann relation and Ballou relation have been employed to evaluate B/A. A comparative study of B/A values obtained from the aforementioned methods has been made. The results are discussed on the basis of structural orientations of normal and branched alkanes.

Keywords. Non-linearity parameter; interaction; structural orientations; acoustic; equimolar binary mixtures; n- or br-alkanes.

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1. Introduction

In the last few years [1–7], a number of theoretical methods have been proposed for estimating the non-linearity parameter (B/A) for pure liquids and liquid mixtures. This parameter has been further correlated with other thermoacoustical parameters [8,9], which are used to deduce the available volume and intermolecular free-length of liquid mixtures [10,11]. Due to the increasing importance of B/A during recent years, an attempt has been made to evaluate B/A of equimolar binary mixtures, viz. chlorobenzene or 1-chloronaphthalene with a series of normal alkanes (n-C_n, n = 6, 8, 10, 12, 14, 16), and with a series of highly branched alkanes (br-C_n, n = 6, 8, 12, 16), viz. 2,2-dimethylbutane (br-C_6), 2,2,4-trimethylpentane (br-C_8), 2,2,4,6,6-pentamethylheptane (br-C_{12}) and 2,2,4,4,6,8,8-heptamethylnonane (br-C_{16}) using Tong and Dong method, thermoacoustical method, Hartmann relation and Ballou empirical relation. A comparative study of B/A values obtained from these relations has also been made in order to review the above-mentioned approaches. Furthermore, the results are discussed in terms of the existence of correlation of

molecular orientations between long chain n- and br-C_n molecules in binary mixtures. The experimental data needed for the estimation of non-linearity parameters of the aforesaid systems have been taken from [12,13].

2. Theoretical

The non-linearity parameter is given by [5]

$$\frac{B}{A} = 2u\rho \left[\frac{\mathrm{d}u}{\mathrm{d}p}\right]_S. \tag{1}$$

Tong and Dong [2] applied Schaaffs equation for the sound velocity in eq. (1) and obtained an equation for B/A as

$$\frac{B}{A} = J(0) + J(x'), \tag{2}$$

where

$$J(0) = \frac{\gamma - 1}{\alpha T} \tag{3}$$

and

$$J\left(x'\right) = \frac{2\left(3 - 2x'\right)^2}{3\left(x' - 1\right)\left(6 - 5x'\right)}, \tag{4}$$

where

$$x' = \frac{V}{b}. \tag{5}$$

Here, ρ is the density, u is the ultrasonic velocity, V is the molar volume, γ is the ratio of specific heats, α is the coefficient of thermal expansion, x' is the real volume of molecule and b is the van der Waals constant. The van der Waals constant b is given by [5]

$$b = \frac{M}{\rho} - \frac{\gamma RT}{u^2}\left[\left\{\sqrt{\frac{Mu^2}{\gamma RT}} + 1\right\} - 1\right]. \tag{6}$$

All the other symbols used have their usual meanings.

General formulation for the non-linearity parameter in terms of the acoustical parameters of liquids has been made using the expression for the sound velocity (u), and introducing the contribution due to isobaric acoustic parameters (K) and the isothermal acoustic parameter (K''). The expression for B/A has been expressed as [14],

$$\frac{B}{A} = 2K + 2\gamma K''. \tag{7}$$

Computations of K and K'' require only the knowledge of thermal expansion coefficient, α. Detailed method of calculation is given in [10,11].

Hartmann and Balizer [15] obtained the following relation for B/A:

$$\frac{B}{A} = 2 + \left(\frac{0.98 \times 10^4}{u}\right), \tag{8}$$

where u is in m s^{-1}.

Empirical relation proposed by Ballou [16] is given by

$$\frac{B}{A} = -0.5 + \left(\frac{1.2 \times 10^4}{u}\right). \tag{9}$$

Experimental data of α, β_{T}, C_{p}, V for liquid mixtures are taken from [12,13], and are further utilized to obtain the corresponding density and ultrasonic velocity with the help of eqs (10) to (12) given below.

$$\beta_{\mathrm{S}} = \beta_{\mathrm{T}} - \frac{\alpha^2 TV}{C_{\mathrm{p}}}, \tag{10}$$

$$\rho = \frac{M}{V}, \tag{11}$$

$$u = \sqrt{\frac{1}{\beta_{\mathrm{S}}\rho}}. \tag{12}$$

3. Results and discussion

Non-linearity parameter for equimolar binary mixtures of chlorobenzene or 1-chloronaphthalene with the series of normal alkanes (n-C$_n$, n = 6, 8, 10, 12, 14, 16) and with a series of highly branched alkanes (br-C$_n$, n = 6, 8, 12, 16), viz. 2,2-dimethylbutane (br-C$_6$), 2,2,4-trimethylpentane (br-C$_8$), 2,2,4,6,6-pentamethylheptane (br-C$_{12}$) and 2,2,4,4,6,8,8-heptamethylnonane (br-C$_{16}$) have been computed with the help of four different methods, viz., Tong and Dong method (eq. (2)), thermoacoustical method (eq. (7)), Hartmann relation, *vide* eq. (8) and Ballou relation, *vide* eq. (9). Experimental data of coefficient of thermal expansion, isothermal compressibility, heat capacity at constant pressure and molar volume for liquid mixtures are taken from [12,13], and have been recorded in table 1. Further, they are utilized to obtain the corresponding density and ultrasonic velocities, *vide* eqs (10) to (12). Computed density and ultrasonic velocity data are then employed to evaluate non-linearity parameter for the various binary systems undertaken for the study. Theoretically calculated B/A values for equimolar binary mixtures, chlorobenzene + n-/br-C$_n$ and 1-chloronaphthalene + n-/br-C$_n$ using the above-mentioned methods are reported in tables 2 and 3 respectively.

A close perusal of table 2 reveals that variations of the calculated B/A values from the thermoacoustical method, Hartmann relation and Ballou relation generally show a decreasing trend with an increase in the number of carbon atoms separately in n-C$_n$ and br-C$_n$ series for binary mixtures of chlorobenzene + n-/br-C$_n$. However, in this case, Tong and Dong method gives a W-shaped variation in

Table 1. Thermodynamic parameters for equimolar binary liquid mixtures chlorobenzene + n-/br-C_n and 1-chloronaphthalene + n-/br-C_n at 298.15 K.

	V (cm^3 mol^{-1})	$\alpha \times 10^3$ (K^{-1})	β_T (T Pa^{-1})	C_p (J mol^{-1} K^{-1})
Chlorobenzene +				
n-C_6	116.41	1.171	1145	174.92
n-C_8	132.77	1.084	1042	202.74
n-C_{10}	149.24	1.023	971	232.99
n-C_{12}	165.62	0.978	917	262.67
n-C_{14}	182.10	0.946	878	292.96
n-C_{16}	198.45	0.921	844	323.48
br-C_6	117.29	1.190	1231	172.04
br-C_8	133.80	1.096	1132	197.68
br-C_{12}	165.96	0.985	996	252.27
br-C_{16}	196.23	0.900	885	306.10
1-Chloronaphthalene +				
n-C_6	132.61	0.944	837.2	203.55
n-C_8	149.10	0.908	795.7	234.08
n-C_{10}	165.57	0.882	767.1	265.48
n-C_{12}	182.07	0.864	747.2	295.92
n-C_{14}	198.57	0.846	727.0	326.68
n-C_{16}	215.01	0.835	710.9	357.28
br-C_6	133.50	0.945	892.7	201.11
br-C_8	150.08	0.904	851.7	227.29
br-C_{12}	182.05	0.846	799.0	281.84
br-C_{16}	213.01	0.795	743.8	335.64

n-C_n series, and a regular decrease from br-C_6 to br-C_{12} followed by an increase for br-C_{16} in br-C_n series. Maximum value of B/A is obtained for chlorobenzene + n-C_6 and chlorobenzene + br-C_6 among the binary mixtures of chlorobenzene + n-C_n and chlorobenzene + br-C_n respectively. In the pure state, the long-chain n-C_n molecules exhibit an orientation order which is short-range, whereas this orientation order is noticeably absent in the case of their branched counterparts because of the fact that orientation order does not occur between the globular-shaped alkanes. The n-alkane molecules form random coils due to internal rotation about the C–C bond, and this tendency increases with increase in chain length. Hence, the extent of coiling in dodecane or hexadecane is more than that of hexane. The presence of chlorobenzene may decrease their coiling and hence molecules acquire their random configuration. Due to greater chain length, the higher alkane molecules provide more favourable accommodation to chlorobenzene molecule in comparison to hexane. The unsymmetrical variation in the n-C_n series may be because of destruction in the order of higher n-C_n molecules. Previously determined V^E values [13] are found to be much larger, especially with C_{16} and it has been suggested that the high predictive values obtained may be due to a packing effect, where chlorobenzene would fit into the available empty regions around the br-C_{16} molecules, which may be considered to be cylindrically shaped. The same discrepancies

Table 2. Non-linearity parameter of equimolar binary liquid mixtures chlorobenzene + n-/br-C_n at 298.15 K.

	B/A			
	eq. (2)	eq. (7)	eq. (8)	eq. (9)
Chlorobenzene +				
n-C_6	9.93	9.46	10.46	9.86
n-C_8	9.05	9.30	10.16	9.50
n-C_{10}	8.85	9.17	9.95	9.24
n-C_{12}	8.90	9.09	9.78	9.02
n-C_{14}	8.82	8.83	10.16	9.49
n-C_{16}	9.27	9.01	9.52	8.70
br-C_6	10.40	9.40	10.76	10.23
br-C_8	9.19	9.22	10.51	9.92
br-C_{12}	8.82	9.03	10.12	9.44
br-C_{16}	9.13	8.93	9.78	9.03

Table 3. Non-linearity parameter of equimolar binary liquid mixtures 1-chloronaphthalene + n-/br-C_n at 298.15 K.

	B/A			
	eq. (2)	eq. (7)	eq. (8)	eq. (9)
1-Chloronaphthalene +				
n-C_6	8.93	9.25	9.74	8.97
n-C_8	9.01	9.17	9.55	8.74
n-C_{10}	9.18	9.10	9.42	8.58
n-C_{12}	9.39	9.06	9.32	8.46
n-C_{14}	9.64	9.03	9.22	8.34
n-C_{16}	9.90	9.02	9.13	8.24
br-C_6	8.88	9.14	10.00	9.30
br-C_8	8.91	9.08	9.82	9.08
br-C_{12}	9.22	8.97	9.61	8.82
br-C_{16}	9.71	8.90	9.40	8.56

are observed in the B/A values, as predicted by Tong and Dong method, in the present investigation also. This validates the superiority of the theory.

For the system 1-chloronaphthalene + n-/br-C_n, the calculated B/A values (table 3) from the three methods (thermoacoustical, Hartmann and Ballou relations) regularly decrease, as we move from n-C_6 to n-C_{16}, and br-C_6 to br-C_{16} separately in the two series of n-C_n and br-C_n. Once again, maximum B/A has been observed from the three methods for 1-chloronaphthalene + n-C_6 and 1-chloronaphthalene + br-C_6. However, Tong and Dong method shows a reverse trend for this binary mixture. In Tong and Dong method, B/A depends on the two contributory terms $J(0)$ and $J(x')$. Due to smaller contribution of the $J(0)$ term to the overall value of B/A, $J(x')$ is important, and this in turn depends on x'. In fact, B/A values are

highly sensitive to the values of x'. Reasonable values of B/A are obtained when x' lies between 1.10 and 1.14. The B/A values for the liquids have been interpreted as the quantity representing the magnitude of the hardness of liquids. The B/A values are concerned with interactions between the components of binary system. Interactions between contributory components of binary mixtures 1-chloronaphthalene +n-/br-C_n are stronger for the lower n- or br-alkanes, becoming smaller for higher alkanes. Previously reported [12] negative V^E values are found to be remarkably large for the lower alkanes and the 1-chloronaphthalene–br-C_6 system experiences a contraction of 1.3% during mixing which reflects the large difference of free-volume between 1-chlorobenzene and br-C_6. Corresponding decreasing magnitude of V^E with increase in n follows as a result of the decreasing free-volume difference and this is indicated by the corresponding B/A values computed by the Tong and Dong method.

The variation of B/A from Tong and Dong method resembles the interaction studies made earlier [12,13] in terms of excess volume and several other mixing functions, for the binary mixtures under investigation, and this confirms the superiority of Tong and Dong method over others.

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