PRAMANA
— journal of
physics

© Printed in India

Vol. 45, No. 3,
September 1995
pp. 221–226

Theoretical calculation of acoustic non-linearity parameter B/A of binary mixtures

J JUGAN, ROSHAN ABRAHAM and M ABDULKHADAR
School of Pure and Applied Physics, Mahatma Gandhi University, Priyadarshini Hill P.O., Kottayam 686 560, Kerala, India

MS received 13 March 1995; revised 21 June 1995

Abstract. Acoustic non-linearity parameter B/A is calculated for five binary liquid mixtures using Tong and Dong equation along with the Flory's statistical theory. Similar to other excess thermodynamical quantities an excess non-linearity parameter $(B/A)^E$ is defined for binary liquid mixtures. The interactions in the liquid mixtures are explained on the basis of the excess non-linearity parameter.

Keywords. Non-linearity parameter; excess non-linearity parameter; binary liquid mixture; ultrasonic velocity; isentropic compressibility.

PACS Nos 43·00; 43·25

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 view point 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 Jie *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.

In the present study, we have calculated the non-linearity parameter of five binary liquid mixtures of benzene, toluene, chlorobenzene, bromobenzene, nitrobenzene and methyl ethyl ketone (MEK), with MEK as a common component. We make use of the Tong and Dong equation [12] for pure liquids and Flory's statistical theory [14, 15] for calculating the B/A values. The thermodynamical parameters in Tong's equation are calculated for binary mixtures using Flory's theory. The variations of B/A with mole fraction of MEK are discussed. Also similar to other thermodynamical parameters, we define an excess non-linearity parameter $(B/A)^E$ for liquid mixtures.

2. Theory

Tong *et al* [12] applied Schaaff's equation for sound velocity in the basic equation for

B/A and obtained the equation.

$$\mathrm{B/A} = J(\mathrm{o}) + J(x) \tag{1}$$

where

$$J(\mathrm{o}) = (1 - 1/\gamma)\frac{c^2 \rho K_T}{T\beta} \tag{2}$$

and

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

Here γ is the ratio of specific heat, ρ is the density, K_T is the isothermal compressibility, T is the temperature, β is the expansibility and x is the real volume of a molecule. x is the ratio of molecular weight to ρb, where b is the van der Waals' constant given by $b = (16/3)\pi r_0{}^3 N$, r_0 being the molecular radius and N the Avogadro number.

In the present study the thermodynamical parameters containing in (2) and (3) and which are required to calculate B/A values of binary mixtures are obtained as follows.

The characteristic and reduced parameters for pure components are obtained from Flory's statistical theory [14, 15] and those of mixtures are calculated by the procedure adopted by Pandey [16, 17]. The thermodynamical parameters β, K_T, C_P and γ for the mixtures which are necessary to calculate B/A for the mixtures are obtained by the relation suggested by Khanwalkar [18]. The van der Waals' constant b and x for the mixtures are calculated as

$$b = y_1 b_1 + y_2 b_2 \tag{4}$$

and

$$x = \frac{y_1 M_1 + y_2 M_2}{\rho_{12} b} \tag{5}$$

where y_1 and y_2 are the mole fractions and M_1 and M_2 are the molecular weights of first and second component respectively and ρ_{12} is the density of the mixture.

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 [19]. Similar to excess thermodynamic functions for binary liquid mixtures we define an excess non-linearity parameter $(\mathrm{B/A})^{\mathrm{E}}$ for binary mixtures as follows:

$$(\mathrm{B/A})^{\mathrm{E}} = (\mathrm{B/A})_{\mathrm{mix}} - (\mathrm{B/A})_{\mathrm{id}} \tag{6}$$

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

$$(\mathrm{B/A})_{\mathrm{id}} = y_1(\mathrm{B/A})_1 + y_2(\mathrm{B/A})_2. \tag{7}$$

Here 1 and 2 refer to first and second components.

The sound velocity, density, adiabatic compressibility and molecular radius required for the present calculations are taken from the literature [20, 21].

3. Results and discussion

Acoustic non-linearity parameter B/A calculated for five binary mixtures at two

Table 1. Mole fraction (y_1) of methyl ethyl ketone, sound velocity (c), isentropic compressibility (K_s), and non-linearity parameter (B/A) of binary mixtures.

	303·15 K			313·15 K		
y_1	c(m/s)	K_s(TPa^{-1})	B/A	c(m/s)	K_s(TPa^{-1})	B/A
		Methyl ethyl ketone + Benzene				
0·0000	1276	707	10·76	1230	770	9·79
0·1126	1269	722	10·34	1226	783	9·52
0·2249	1260	739	9·97	1217	802	9·29
0·3113	1253	753	9·72	1210	817	9·14
0·4163	1244	771	9·46	1201	837	8·99
0·5232	1234	791	9·23	1191	859	8·88
0·6045	1225	809	9·08	1182	878	8·83
0·7148	1212	835	8·92	1169	908	8·81
0·8265	1197	865	8·83	1154	941	8·88
1·0000	1173	915	8·81	1128	1002	9·20
		Methyl ethyl ketone + Toluene				
0·0000	1291	699	11·62	1248	757	10·44
0·1367	1281	716	10·98	1240	773	9·99
0·2214	1274	728	10·61	1233	786	9·72
0·3435	1263	746	10·13	1222	807	9·39
0·4318	1255	761	9·81	1214	822	9·19
0·5406	1243	782	9·47	1202	846	8·98
0·6267	1232	801	8·85	1191	867	8·85
0·7122	1219	824	9·03	1178	893	8·78
0·8178	1203	855	8·86	1162	927	8·78
1·0000	1173	915	8·81	1128	1002	9·20
		Methyl ethyl ketone + Chlorobenzene				
0·0000	1245	589	12·02	1206	634	10·85
0·1068	1238	611	11·40	1197	660	10·41
0·1972	1235	629	10·97	1194	679	10·09
0·3202	1229	656	10·41	1188	709	9·68
0·4174	1224	680	10·01	1183	736	9·39
0·5576	1218	718	9·55	1177	776	9·06
0·6242	1213	740	9·37	1172	801	8·94
0·7288	1201	782	9·06	1160	848	8·81
0·8531	1187	840	8·84	1146	911	8·80
1·0000	1173	915	8·81	1128	1002	9·20
		Methyl ethyl ketone + Bromobenzene				
0·0000	1146	514	11·70	1109	554	10·80
0·1221	1144	542	11·10	1104	587	10·35
0·1917	1141	562	10·80	1101	609	10·09
0·2946	1139	591	10·41	1099	641	9·77
0·4069	1142	623	10·02	1102	676	9·46
0·5335	1146	665	9·59	1106	721	9·15
0·6748	1152	721	9·19	1112	782	8·89
0·8126	1155	796	8·90	1115	863	8·80
1·0000	1173	915	8·81	1128	1002	9·20

(*Continued*)

Table 1. (*Continued*)

	303·15 K			313·15 K		
y_1	c(m/s)	K_s(TPa^{-1})	B/A	c(m/s)	K_s(TPa^{-1})	B/A
		Methyl ethyl ketone + Nitrobenzene				
0·0000	1456	395	14·20	1408	426	12·71
0·0986	1426	424	13·15	1386	452	12·05
0·2098	1388	463	12·27	1348	494	11·31
0·3268	1154	506	11·42	1314	542	10·58
0·4182	1236	537	10·84	1296	575	10·08
0·5212	1312	579	10·24	1272	621	9·64
0·6458	1277	642	9·64	1239	691	9·15
0·7512	1241	715	9·19	1201	771	8·87
0·8119	1223	759	8·99	1183	819	8·78
1·0000	1173	915	8·81	1128	1002	9·20

different temperatures are given in table 1. The table also contains B/A of pure liquids. 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 the hardness of the liquid [6] which may be considered to be true for the liquid mixtures as well. For all the five mixtures, as the mole fraction of MEK increases, the density and ultrasonic velocity decrease and hence the compressibility increases. Therefore as the mole fraction of MEK increases the bulk modulus, hence B/A must decrease.

Subramanyam Reddy [20] reported that the excess isentropic compressibility for all the five binary mixtures considered in the present study are negative. A plot of the calculated excess B/A, $(B/A)^E$, against mole fraction of MEK in the mixtures is shown in figure 1. It is interesting to note that $(B/A)^E$ values are all negative and show the same trend as that of the reported excess isentropic compressibility [20]. A negative compressibility is an indication of strong interaction in the liquid mixtures [22], which has been attributed to charge transfer, dipole-induced dipole and dipole-dipole interaction while a positive sign indicating weak interaction has been interpreted as due to dispersion forces [23]. In MEK-benzene system there is a dipole interaction between π electrons in the benzene ring and the carbonyl group $\rangle$Co of MEK. Also in MEK-toluene there is dipole interaction between $\rangle$CO and CH_2 group. In the other mixtures the same type of interactions are present between $\rangle$CO and –Cl, –Br or $-NO_2$. The difference in the magnitude of $(B/A)^E$ for different mixtures is attributable to the difference in the extent of interactions present in them. It may be inferred that a more negative value of $(B/A)^E$ indicates a strong interaction between the different groups in the system. This is in accordance with the results of the study of excess isentropic compressibility values [20].

4. Conclusion

Acoustics non-linearity parameter B/A is calculated for five binary mixtures with methyl ethyl ketone as common component at two different temperatures. An excess

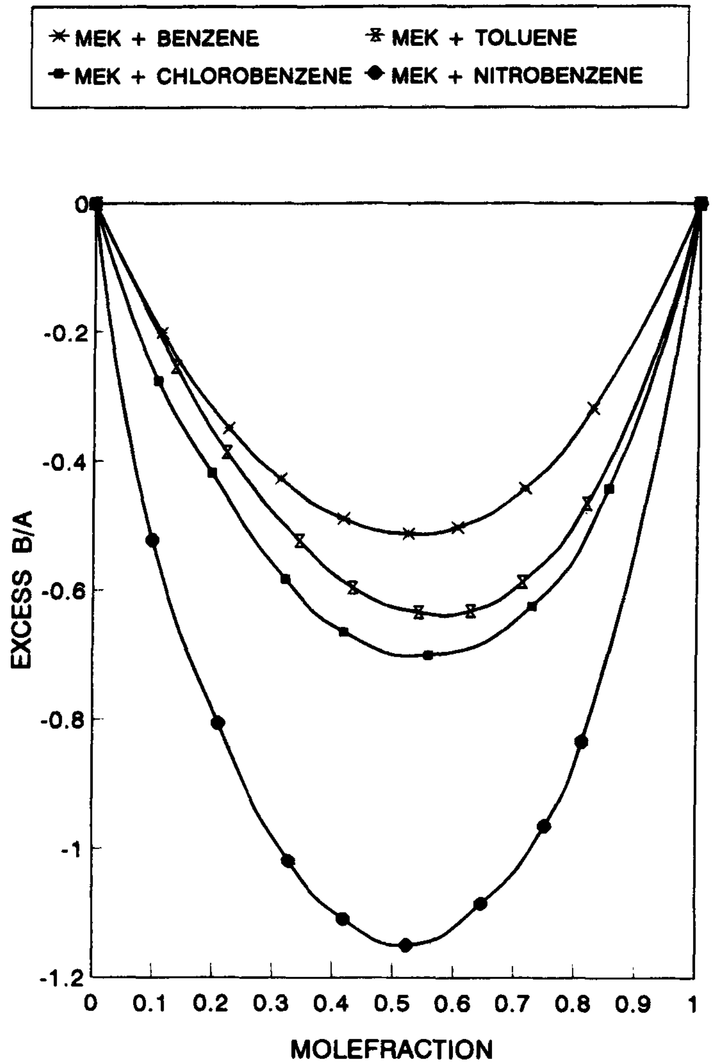

Figure 1. Variation of excess B/A with mole fraction of methyl ethyl ketone at 303·15 K.

non-linearity parameter $(B/A)^E$ which shows the same type of variation as isentropic compressibility with mole fraction has been defined. It is concluded that the $(B/A)^E$ is also an important quantity similar to other thermodynamic parameters useful to explaining the interaction in binary liquid mixtures.

References

[1] M Paul Hagelberg, *J. Acoust. Soc. Am.* **41**, 564 (1967)
[2] A B Coppens and Robert T Beyer, *J. Acoust. Soc. Am.* **38**, 797 (1965)

[3] Charles A Cain, *J. Acoust. Soc. Am.* **80**, 685 (1986)
[4] Harumi Endo, *J. Acoust. Soc. Am.* **71**, 330 (1986)
[5] B K Sharma, *J. Acoust. Soc. Am.* **73**, 106 (1983)
[6] Harumi Endo, *J. Acoust. Soc. Am.* **83**, 2043 (1988)
[7] Wesley N Cobb, *J. Acoust. Soc. Am.* **73**, 1525 (1983)
[8] Chandra M Sehgal and Burdett R Porter, *J. Acoust. Soc. Am.* **79**, 566 (1986)
[9] Laszlo Alter and E A Hiedemann, *J. Acoust. Soc. Am.* **34**, 410 (1962)
[10] A P Sarvazyan and T V Gnalikian, *J. Acoust. Soc. Am.* **88**, 1555 (1990)
[11] W K Law and L A Frizzell, *J. Acoust. Soc. Am.* **74**, 1295 (1983)
[12] Tong Jie and Dong Yanwu, *Kexue Togbao* **33**, 1511 (1988)
[13] W Schaaffs, *Z. Phys.* **115**, 69 (1940)
[14] P J Flory, *J. Am. Chem. Soc.* **87**, 1833 (1965)
[15] A Abe and P J Flory, *J. Am. Chem. Soc.* **87**, 1838 (1965)
[16] J D Pandey, *J. Chem. Soc. Faraday Trans. I* **75**, 2160 (1979)
[17] J D Pandey, *J. Chem. Soc. Faraday Trans. II* **76**, 1215 (1980)
[18] M S Khanwalkar, *Acoust. Lett.* **13**, 121 (1990)
[19] Shao-muMa and Henry Eyring, *J. Chem. Phys.* **42**, 1920 (1965)
[20] K Subramanyam Reddy, *J. Chem. Eng. Data* **31**, 238 (1986)
[21] S Ernst and J Glinski, *Acustica* **48**, 109 (1981)
[22] R J Fort and W R Moore, *Trans Faraday Soc.* **61**, 2102 (1965)
[23] K Sivanarayanan and S Prakash, *Acustica* **50**, 286 (1982)