

Evaluation of Non-Linearity (B/A) Parameters of Multicomponent Liquid Systems



Chemistry

KEYWORDS :

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ABSTRACT

Non linearity parameter (B/A) for ternary liquid mixtures of (ethanol+N,N-DMF+cyclohexane) at 298.15 K and (n-pentane+n-hexane+benzene) at 308.15 K have been calculated by three different methods viz. Beyers, Hartmann and Ballou. Non-linearity parameter is related with thermoacoustical quantities like isobaric acoustical parameter (K), isothermal acoustical parameter (K'), isochoric acoustical parameter (K'') and isothermal and adiabatic compressibility ratio (γ) which depend upon thermal expansion coefficient (α), Sharma parameter (S*) and isochoric temperature coefficient of internal pressure (X). All above parameters were calculated by using density and ultrasonic velocity values of multicomponent liquid mixtures. In ternary liquid mixture (n-pentane+n-hexane+benzene), the non-linearity parameter (B/A) values obtained by all three methods are very close to each other but in case of (ethanol+N,N-DMF+cyclohexane), the values by Hartmann and Ballou are close whereas by Beyer's they are different.

INTRODUCTION

When sound waves of high intensity are made to propagate into the fluids then acoustic non-linear effect occurs due to great attenuation of high frequency component compared to low frequency ones. When sound wave of high amplitude are propagated in gases and liquids, several non-linear effects such as frequency distortion and acoustic scattering occur causing the measurement of ultra propagation constant to be unreliable [1]. These non-linear effects can be expressed by non-linear terms in the equation of wave propagation. These non-linear effects arise due to higher attenuation of the high frequency components. The non-linear departure of the propagation process is symbolized by the factor B/A which is called non-linearity parameter. This parameter gives valuable informations like intermolecular spacing, internal pressure clustering etc. Non-linearity parameter plays vital role in non-linear acoustics.

In past a number of theoretical and experimental investigations have been made. Beyer's [1-4], Nomoto [5], Kor et al [6], Swami et al [7], Jugun et al [8] computed non-linearity parameter (B/A) for a number of liquids and liquid solutions making use of thermodynamic method. Non-linearity parameter of higher cycloalkanes was estimated at varying temperature and pressures by Verma et al [9]. Pandey et al [10-14] determined B/A values of pure binary and some ternary liquid mixtures. B/A values for amino acids, proteins, tissues and different biological samples have been studied [15]. The necessary experimental data used for the calculation of B/A have been taken from literature [16-18]. In the present work non-linearity parameters (B/A) of ternary liquid mixtures of (ethanol+N,N-DMF+cyclohexane) and (n-pentane+n-hexane+benzene) have been calculated using Beyers, Hartmann [19] and Ballou methods.

EXPERIMENTAL

The solvents were purified by standard procedures and all the chemicals used were of AR grade. Density of the system under investigation was measured using single-limbed pycnometer with bulb capacity of approximately 10^{-5} m^3 volume. The accuracy in the measurement of the density was $\pm 0.01 \text{ kg m}^{-3}$. Ultrasonic velocity was measured at a fixed frequency of 2 MHz using ultrasonic interferometer supplied by Mittal Enterprises (New Delhi) with an accuracy of $\pm 0.03\%$.

THEORETICAL

Beyer's non-linearity parameter B/A, which is combination of the temperature and pressure derivatives of ultrasonic velocity can be expressed as [20]

$$\frac{B}{A} = \left(\frac{2Mu^2}{V} \right) \left(\frac{d \ln u}{dP} \right)_T + \left(\frac{2Mu^2 \alpha T}{C_p} \right) \left(\frac{d \ln u}{dT} \right)_P$$

$$= 2K' - 2K(\gamma - 1) \left(1 - \frac{K'}{K} \right) = 2K - 2\gamma \Gamma'$$

Data on temperature and pressure dependence on bulk modulus (Warfield 1974), (Hartman 1975) show that

$$\Gamma'' = -K''$$

which is negative quantity. Thus,

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

where K, K', K'' and γ are the isobaric, isothermal, isochoric acoustical parameters and heat capacity ratio respectively and the values of these parameters have been evaluated by methods suggested earlier. K and K'' can be expressed as

$$K = - \left(\frac{1}{\alpha} \right) \left(\frac{d \ln u}{dT} \right)_P = \frac{1}{2} \left[1 + \frac{S^*(1 + \alpha T)}{\alpha T} \right] = K' \cdot K''$$

$$K'' = - \frac{1}{\alpha} \left(\frac{d \ln u}{dT} \right)_P = 1 + \left(\frac{X}{2\alpha T} \right) = K' \cdot K$$

Sharma parameter (S*), reduced volume (\tilde{V}), isochoric temperature coefficient of internal pressure (X) and Moelwyn - Hughes parameters (C1) are given as

$$S^* = 1 + \frac{4\alpha T}{3}$$

$$\tilde{V} = \left[1 + \frac{\alpha T}{3(1 + \alpha T)} \right]^3 = \left(\frac{S^*}{1 + \alpha T} \right)^3$$

$$X = \left(\frac{d \ln P_m}{d \ln T} \right)_P = - \frac{2S^* S_0^*}{\tilde{V}^{C_1}} = -2 \frac{(1 + 2\alpha T)}{\tilde{V} C_1}$$

$$C_1 = \left(\frac{d \ln \alpha}{d \ln T} \right)_P = \frac{13}{3} + \frac{1}{\alpha T} + \frac{4\alpha T}{3}$$

Thermal expansion coefficient and isothermal compressibility have been evaluated as

$$\alpha = \frac{75.6 \times 10^{-3}}{T^{1/2} u^2 \rho^{1/2}}, \text{ K}^{-1}$$

$$\beta_T = \frac{1.71 \times 10^{-3}}{T^{1/2} u^2 \rho^{1/2}}, \text{ cm}^{-2} \text{ dyne}^{-1}$$

where u is in ms^{-1} and ρ is in g cm^{-3}

Adiabatic compressibility is obtained by the equation

$$\beta_s = \frac{1}{u^2 \rho}$$

and heat capacity ratio (γ) have been calculated by the equation

$$\gamma = \frac{\beta_T}{\beta_S}$$

Ultrasonic velocity in liquid is affected by intermolecular interaction. It is assumed that potential energy dominates in determining ultrasonic velocity in liquids. It is obvious that the thermal pressure contribution to the ultrasonic velocity is negligible in comparison to the internal pressure contribution. This approach approximately predicts qualitatively accurate results. Under these assumptions, Hartmann theoretically derived an expression for B/A as

$$\frac{B}{A} = 2 + \frac{(0.98 \times 10^4)}{u}$$

and Ballou also proposed the following relation for B/A

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

where u is the ultrasonic velocity in ms⁻¹

RESULT AND DISCUSSION:

Non-linearity parameter (B/A) of ternary mixture of (ethanol + N,N-DMF + cyclohexane) at 308.15 and (n-pentane + n-hexane + benzene) at 298.15 have been computed by using three different methods namely by Beyer's, Hartmann and Ballou. These computed values are reported in table -1 and 2. The data ultrasonic velocity and density required for the present computation have been taken from the literature [16-18]. In Beyer's method, isobaric (K), isochoric acoustical parameter (K'') and heat capacity ratio (γ) have also been calculated which are also reported in tables. The values of table -1 reveal that the non-linearity parameters (B/A) obtained by Hartmann and Ballou methods are very close to each other and decrease slightly from top to bottom as mole fraction of ethanol increases. This is due to the fact that non-linearity parameter by both the methods depends only upon ultrasonic velocity which increase from top to bottom and present in the denominator of the formula. But non-linearity parameter by Beyer's method slightly increases as the mole fraction of ethanol increases. Since they depend upon both density and ultrasonic velocity. These values are different from other non-linearity values. The fig.1 ensures the above results.

Table 1- Non-linearity parameter by different methods of ternary liquid mixture: Ethanol (x1) + N,N-DMF (x2) + Cyclohexane (x3) at 308.15

x1	x2	rm (g cm ⁻³)	u _m (m s ⁻¹)	K	K''	γ	B/A Beyer's	B/A Hartmann	B/A Ballou
0.0703	0.0704	0.7691	1195	3.2111	5.1263	1.4618	21.41	10.20	9.88
0.1232	0.1234	0.7762	1194	3.2138	5.1407	1.4573	21.41	10.21	9.89
0.1451	0.1455	0.7792	1195	3.2156	5.1500	1.4554	21.42	10.20	9.88
0.2056	0.2059	0.7894	1197	3.2209	5.1785	1.4492	21.45	10.19	9.86
0.2416	0.2420	0.7978	1203	3.2272	5.2120	1.4440	21.51	10.15	9.81
0.3071	0.3076	0.8133	1222	3.2423	5.2925	1.4348	21.67	10.02	9.65
0.3940	0.3949	0.8349	1249	3.2637	5.4066	1.4223	21.91	9.85	9.43
0.4305	0.4314	0.8479	1264	3.2761	5.4727	1.4150	22.04	9.75	9.31
0.4675	0.4682	0.8609	1285	3.2912	5.5535	1.4079	22.22	9.63	9.15

Table 2- Non-linearity parameter by different methods of ternary liquid mixture: n-Pentane (x1) + n-Hexane(x2) + Benzene (x3) at 298.15

x1	x2	rm (g cm ⁻³)	u _m (m s ⁻¹)	K	K''	γ	B/A Beyer's	B/A Hartmann	B/A Ballou
0.0966	0.4171	0.7432	1201.1	3.2324	0.5244	1.5004	8.04	10.16	9.82
0.1428	0.3739	0.7416	1197.5	3.2300	0.5249	1.5015	8.04	10.18	9.85
0.2017	0.3388	0.7361	1193.2	3.2255	0.5258	1.5052	8.03	10.21	9.89
0.2590	0.3038	0.7286	1187.7	3.2196	0.5271	1.5104	8.03	10.25	9.94
0.2984	0.2877	0.7218	1177.2	3.2118	0.5288	1.5151	8.03	10.32	10.03
0.3075	0.2945	0.7195	1175.2	3.2098	0.5292	1.5167	8.02	10.34	10.05
0.3420	0.3143	0.7073	1173.4	3.2032	0.5306	1.5254	8.03	10.35	10.07
0.3685	0.3523	0.6953	1170.2	3.1961	0.5322	1.5341	8.03	10.37	10.10
0.4082	0.4665	0.6688	1163.2	3.1803	0.5357	1.5541	8.03	10.43	10.16
0.4099	0.3888	0.6838	1178.4	3.1940	0.5327	1.5427	8.03	10.32	10.02

In table-2, the non-linearity parameter (B/A) obtained by all the three methods in case of ternary liquid mixtures (n-pentane + n-hexane + benzene) have been reported. Since ultrasonic velocity slightly decreases as mole fraction of n-pentane increases, so non-linearity parameter obtained by Hartmann and Ballou methods slightly increases from top to bottom. But the non-linearity parameter obtained by Beyer's method which depend on both density and ultrasonic velocity are almost constant. The aforesaid results can be ensured by fig.2

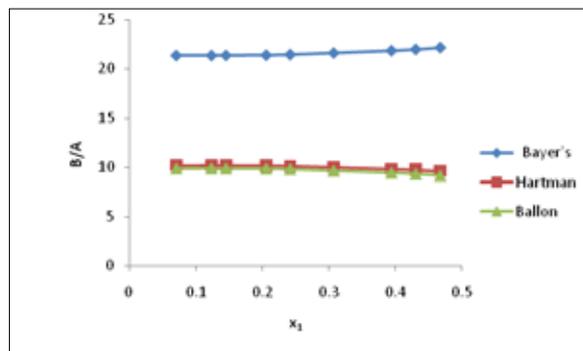


Fig.1. Ethanol (x₁) + N,N-DMF (x₂) + Cyclohexane (x₃) at 308.15

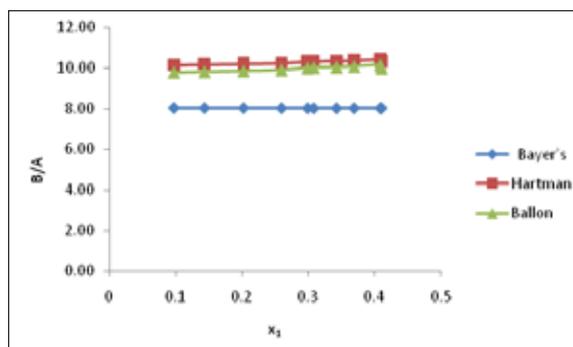


Fig.2. n-Pentane (x₁) + n-Hexane(x₂) + Benzene (x₃) at 298.15

ACKNOWLEDGEMENT :

We are thankful to the Principal, Head, department of chemistry, KNIPSS, Sultanpur for providing useful facilities.

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