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Non-Linearity Parameter B/A of Pure Organic Liquids

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Abstract : Non-linearity parameter, B/A, of twelve organic liquids have been theoretically computed over a wide range of temperature. Use has been made of the equation proposed by Tong and Dong which incorporates the Schaaffs proposal in conjunction with Van der Waals equation. For all the concerned liquids, B/A value have been found of quite satisfactory.

The importance of non-linearity parameter (B/A) lies in obtaining information about the errors in absorption measurements produced by the presence of finite amplitude sound waves and physical attributes of liquids such as internal pressure and acoustic scattering[1,2]. Various experimental and theoretical studies have been performed on non-linearity parameters of liquids using phenomenological[3,5] or thermodynamic methods[6,7]. Also some studies on B/A have been carried out from the point of view of theory of liquids[8]. Further, B/A values for amino acids, proteins, tissues, different biological samples[9,10], alcohols and other organic liquids at different temperatures[4,5,11] have been studied. Since acoustic properties of biological media have been taken as those of simple liquids[12], investigation leading to relation between B/A and molecular structure of simple liquids will prove to be the first step towards studying this relation in biological media. This paper is exclusively concerned with deduction of relation between B/A and molecular volume according to Schaaff's hypothesis based on Vander Waals equation. For the present investigation, the twelve pure organic liquids whose B/A have been measured are acetone, methyl iodide, cyclohexane, o- xylene, m-xylene, p-xylene, tetrahydropyran, piperidine, n- pentane, n-decane.

1. Theory

When sound waves of finite amplitude pass through fluids, they give rise to a number of non-linear phenomenon such as wave attenuation, harmonic distortion and sound saturation. In 1939, Schaaff's[13] proposed that acoustic velocity in organic liquids was related to its molecular structure and took the help of Vander Waals equation,

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

where M is the molecular weight, γ the ratio of specific heats and b the Van der Waals constant given by

$$b = \frac{16}{3} . \pi r_0^3 N .$$

where r_0 is the molecular radius of organic liquid and N the Avogadro's number.

Tong *et al.*[14] applied Schaaff's equation for sound velocity and obtained an expression for non-linearity parameter B/A as

$$B/A = J(0) + J(x)$$

where

$$J(0) = \left(1 - \frac{1}{\gamma}\right) . \frac{u^2 . \rho \beta_T}{\alpha . T} \quad \text{and} \quad J(x) = \frac{2(3 - 2x)^2}{3(x - 1)(6 - 5x)}$$

where $x = \dfrac{M}{\rho . b}$ and all the symbols have their usual meaning.

At atmospheric pressure and room temperature, for most organic liquids.

$\beta_T \cong 10^{-10} (m^2/N)$ in order of magnitude.

$\alpha = 0.5 \times 10^{-3}$ to 1.7×10^{-3} K^{-1}.

$\gamma = 1$ to 1.5 and

$u \leq 1.5 \times 10^3$ m/sec.

Thus, $J(0) \cong 0$ to 1.5.

2. Results and Discussion

With the help of the formula derived by Tong and Dong[14], which has been used in this chapter, B/A has been calculated for twelve pure organic liquids viz., acetone, methyl iodide, cyclohexane, *o*-xylene, *m*-xylene, *p*-xylene, tetrahydropyran, piperidine, *n*-pentane, *n*-hexane, *n*-heptane and *n*-decane. The experimental values of parameters used in the computation have been taken from literature[15-18]. B/A of all the twelve pure organic liquids have been computed in the Table 1-4, along with the necessary thermodynamic data. From microscopic thermodynamic parameters, Endo[6] deduced a formula for B/A in form of the polynomial of $(\gamma - 1)$. He pointed out that the values of B/A computed by this formula is around 8 for many liquids which is little smaller than the experimental value.

Nomoto[19] and Hartmann[20] have studied B/A using their own hypothesis and their results give B/A = 6 for liquids. Nomoto used Rao's[21] liquid model for all the liquids which is effective to very few liquids like water, while Hartmann's inner energy was only attributed to potential energy between molecules and the molecular thermal kinetic energy was neglected. As a result of this, the B/A values of the liquids expected by them were all lower than the experimental ones.

Table 1 : Computed values of B/A for Acetone and Methyl iodide at various tempertures

T (°K)	ρ (gm / cc)	u (m / sec)	J (0)	J (x)	B / A
Acetone					
253.2	0.834	1365	1.20	8.01	9.21
263.2	0.823	1321	1.12	8.09	9.21
273.2	0.813	1275	1.06	8.33	9.39
283.2	0.801	1230	0.98	8.77	9.75
193.2	0.790	1185	0.91	9.59	10.50
303.2	0.779	1140	0.84	11.19	12.03
308.2	0.774	1117	0.82	12.86	13.68
Methyl Iodide					
253.2	2.390	944	1.81	8.00	9.81
263.2	2.362	918	1.85	8.07	9.92
273.2	2.334	892	1.68	8.23	9.91
283.2	2.306	866	1.59	8.55	10.14
293.2	2.278	840	1.51	9.06	10.57
303.2	2.249	814	1.40	9.94	11.34
308.2	2.234	801	1.35	10.63	11.98

Table 2 : Computed value of B/A for Cyclohexane, o-xylene, m-xylene and p-xylene at various temperatures

T (°K)	ρ (gm / cc)	u (m / sec)	J (0)	J (x)	B / A
Cyclohexane					
298.15	0.774	1249.5	0.95	8.06	9.01
313.15	0.759	1177.5	0.86	8.01	8.87
323.15	0.750	1129.2	0.12	8.03	8.15
o-xylene					
298.15	0.876	1349.8	0.97	8.96	9.93
313.15	0.863	1290.4	0.87	8.63	9.50
323.15	0.855	1250.8	0.81	8.44	9.26
m-xylene					
298.15	0.860	1323.4	1.01	8.81	9.82
313.15	0.847	1258.3	0.89	8.49	9.38
323.15	0.838	1216.7	0.83	8.30	9.13
p-xylene					
298.15	0.857	1309.7	0.96	8.78	9.74
313.15	0.844	1248.3	0.87	8.46	9.33
323.15	0.835	1207.4	0.81	8.28	9.09

Table 3 : Computed values of B/A for Piperidine, Tetrahydropyran and Cyclohexane at various temperatures

T (°K)	ρ (gm / cc)	u (m / sec)	J (0)	J (x)	B / A
Piperidine					
293.15	0.861	1379.8	0.96	8.44	9.38
303.15	0.852	1337.0	0.89	8.27	9.16
313.15	0.843	1294.2	0.83	8.13	8.97
323.15	0.834	1251.4	0.77	8.04	8.81
333.15	0.825	1208.6	0.72	8.00	8.72
Tetrahydropyran					
293.15	0.874	1291.2	1.08	8.11	9.20
303.15	0.864	1246.4	1.00	8.03	9.03
313.15	0.854	1201.7	0.92	8.00	8.92
323.15	0.844	1156.9	0.84	8.05	8.89
333.15	0.834	1112.2	0.77	8.22	8.99
Cyclohexane					
293.15	0.779	1273.8	1.09	8.08	9.17
303.15	0.769	1225.7	0.99	8.01	9.00
313.15	0.760	1177.6	0.91	8.01	8.92
323.15	0.750	1129.5	0.82	8.12	8.94
333.15	0.741	1081.4	0.74	8.39	9.14

Table 4 : Computed values of B/A for some normal paraffins at various temperatures

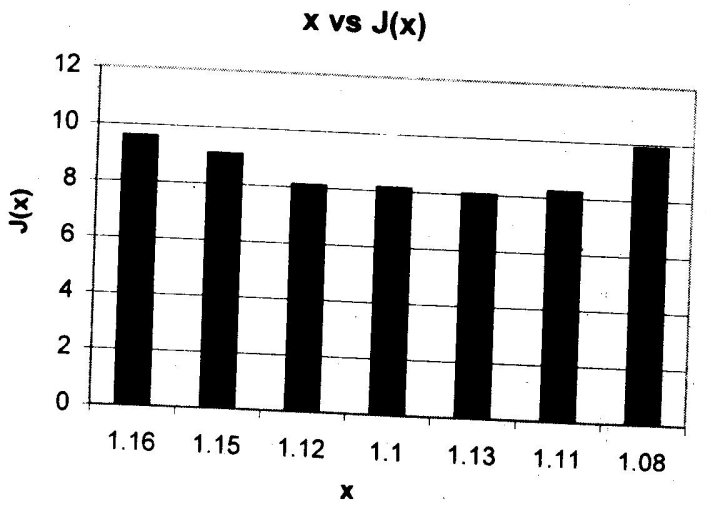
T (°K)	ρ (gm / cc)	u (m / sec)	J (0)	J (x)	B / A
n-pentane					
283.15	0.645	1076.1	0.97	8.45	9.24
288.15	0.641	1052.5	0.76	8.78	9.54
295.15	0.647	1019.5	0.74	9.53	10.26
303.15	0.625	981.9	0.67	11.06	11.74
n-hexane					
293.15	0.671	1097.6	0.75	8.01	8.75
313.15	0.653	1007.1	0.64	8.45	9.10
333.15	0.636	916.9	0.54	10.87	11.41
n-heptane					
293.15	0.693	1151.9	0.75	8.23	8.98
313.15	0.675	1067.1	0.66	8.01	8.66
333.15	0.658	982.5	0.57	8.19	8.76
353.15	0.639	897.5	0.49	9.58	10.07

T (°K)	ρ (gm / cc)	u (m / sec)	J (0)	J (x)	B / A
n-decane					
293.15	0.739	1249.4	0.74	9.88	10.62
313.15	0.724	1175.3	0.66	9.24	9.90
33.15	0.709	1101.2	0.59	8.70	9.28
353.15	0.693	1027.1	0.51	8.28	8.79
363.15	0.685	990.1	0.47	8.13	8.60

A plot of x *vs* $J(x)$ (Table 5) reveals that the minimum value of $J(x)$ is 8. Comparison of $J(0)$ and $J(x)$ further indicates that the $J(0)$ can only be 16% of B/A at maximum. Thus, B/A is mostly determined by x which represents the ratio of molar volume to the real volume of a mole of molecules and furthermore the values of B/A is always greater than 8.

Table 5 : A plot of x *vs* $J(x)$ values for the various pure liquids

Liquid	x	J (x)
Acetone	1.16	9.587
Cyclohexane	1.15	9.058
Tetrahydropyran	1.12	8.078
Piperidine	1.10	8.114
n-Hexane	1.13	8.006
n-Heptane	1.11	8.226
n-Decane	1.08	9.878



Another interesting thing to note is that $J(0)$ contributes only 16% to overall value of B/A and thus B/A values are largely dependent on $J(x)$, which in turn depends on x. Even minute changes in x affects the value of $J(x)$ to a great extent. Thus for values of x exceeding 1.5 and 1.2 very absurd values are obtained, due to the terms $(3 - 2x)$ and $(6 - 5x)$ in numerator and denominator respectively. Another interesting feature was that good values of $J(x)$ result when x lies between 1.10 and 1.14.

From the above discussions, we conclude that for most organic liquids at room temperature and atmospheric pressure, values of acoustic non-linearity parameter are larger than 8. We also see that in organic liquids, the values of B/A are mainly attributed to the ratio of molar volume to the real volume of the molecules in one mole of the liquid.

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