

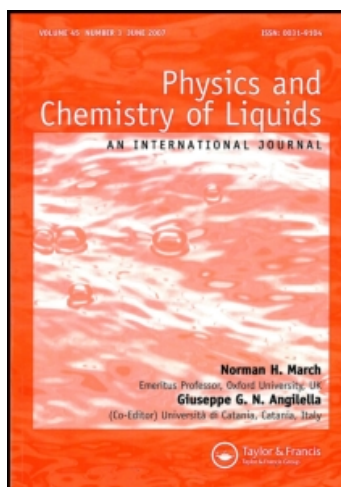
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ACOUSTIC NONLINEARITY PARAMETER OF LIQUID ALKANES AS A FUNCTION OF TEMPERATURE, CHAIN LENGTH AND ISOMERISM

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The acoustic nonlinearity parameter B/A along with intermediate quantities such as the pressure derivative of sound speed and the phase shift were measured in 8 linear alkanes and a series of four isomers of hexane. The influences of temperature and chain length on these quantities were revealed. It was found that the phase shift parameter is more sensitive to molecular structure and temperature than B/A and that the pressure derivative of sound speed.

Keywords: Linear alkanes; Sound speed

1. INTRODUCTION

Experimental and theoretical studies indicated that the acoustic nonlinearity parameter B/A is related to internal pressure [1], hardness [2], intermolecular potential [3], molecular structure [4–9] and molecular interaction [1, 10] of liquids. It has also been shown that the nonlinearity parameter B/A , Rao's exponent, and the anharmonic Gruneisen parameter are related to each other [3, 11, 12]. From its definition, the nonlinearity parameter B/A [13] is closely associated

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with many basic thermodynamic parameters such as density ρ , specific heat capacity at constant pressure C_p , the volume thermal expansive coefficient α , and sound speed c ; thus it can be considered as a thermodynamic parameter. Moreover, B/A displays the dynamic properties of the material [14], and can reflect the change of state or structure [7, 9, 15] in the matter. All of these distinguishing features of B/A mean that it can be used as a complementary parameter for characterization of liquids, and further develop modern theory of liquid.

The fact that there are a large number of organic liquid families, with different but similar molecular structures, suggests the need to choose a small number of specific organic liquid families to studying the influence of molecular structure on B/A . In this paper, the experiment was performed for an organic liquid family, *i.e.*, linear alkanes and an isomer series. The B/A values along with the intermediate quantities such as the pressure derivative of sound speed and phase shift parameter as a function of temperature were measured. The influences of temperature and molecular structure on these quantities were revealed and discussed.

2. EXPERIMENTAL TECHNIQUE

The parameter of nonlinearity B/A is derived from the Taylor series expansion of the instantaneous pressure $P(\rho, s)$ around equilibrium conditions (P_0, ρ_0) along an isentropic process

$$P = P_0 + \left(\frac{\partial P}{\partial \rho} \right)_s (\rho - \rho_0) + \left(\frac{\partial^2 P}{\partial \rho^2} \right)_s \frac{(\rho - \rho_0)^2}{2!} + \left(\frac{\partial^3 P}{\partial \rho^3} \right)_s \frac{(\rho - \rho_0)^3}{3!} + \dots \quad (1)$$

which can be rewritten as:

$$P = P_0 + A \left(\frac{\rho - \rho_0}{\rho_0} \right) + \frac{B}{2} \left(\frac{\rho - \rho_0}{\rho_0} \right)^2 + \frac{C}{6} \left(\frac{\rho - \rho_0}{\rho_0} \right)^3 + \dots \quad (2)$$

where the temperature-dependent parameters, A , B , and C are defined by:

$$A = \rho_0 \left(\frac{\partial P}{\partial \rho} \right)_s = \rho_0 c_0^2 \quad (3)$$

$$B = \rho_0^2 \left(\frac{\partial^2 P}{\partial \rho^2} \right)_s = 2\rho_0^2 c_0^3 \left(\frac{\partial c}{\partial P} \right)_s \quad (4)$$

$$C = \rho_0^3 \left(\frac{\partial^3 P}{\partial \rho^3} \right)_s \quad (5)$$

c_0 being the sound velocity. Therefore, the acoustic nonlinearity parameter B/A is expressed in the following form:

$$B/A = 2\rho_0 c_0 \left(\frac{\partial c}{\partial P} \right)_s \quad (6)$$

which shows that B/A is a thermodynamic property proportional to second order derivative of density with pressure.

The technique deployed to carry out measurements of the change of sound speed caused by the change of pressure, which rests on the improved thermodynamic method, uses a highly sensitive phase comparison technique. The experimental apparatus, which has already been described in detail in a previous paper [16], is composed of a cell with two PZT transducers immersed in the fluid. When the distance d between transmitting transducer and receiving transducer is fixed, $c = d/t$ where c is the sound velocity of the medium tested and t the travel time. As the variation of sound velocity Δc is equivalent to the variation of travel time from transmitter to receiver $\Delta t = -(d/c^2)\Delta c$ or equivalent to the phase shift of sound wave $\Delta\phi = \omega\Delta t$, then from Eq. (6), the nonlinearity parameter can be obtained as

$$B/A = -\frac{2\rho c^3}{\omega d} \left(\frac{\Delta\phi}{\Delta P} \right)_s \quad (7)$$

Thus, the measurement of nonlinearity parameter B/A has been turned into the measurement of variation of phase difference between two coherent signals caused by the change in static pressure. The isentropic condition in Eq. (7) can be realised by arranging the measurement process to take place so rapidly (1–2 seconds) and the change of pressure to be small enough (1–2 atmospheres) that there is no significant thermal conduction near the acoustic path in the test cell.

3. THE MEASUREMENT FOR LINEAR ALKANES

The organic liquid family chosen is that of linear alkanes. It is well known that linear alkanes have the molecular structure of straight chains with the general chemical formula $\text{CH}_3\text{—}[\text{CH}_2]_{n-2}\text{—CH}_3$, where n is the number of carbon atoms in the chain and is called the chain length. When n increases, a —CH_2 group is added to the straight chain of linear alkanes. The experiments were carried out for 8 linear alkanes (supplied by the FLUKA company with a purity greater than 99%) ranging from hexane to tridecane in the liquid state in 10 K intervals between 283.15 and 353.15 K. All the $(\Delta c/\Delta P)_S$ values measured are displayed on Table I. The variations of this property

TABLE I Pressure derivative of sound speed and related parameters for linear alkanes at various temperatures

Carbon number	283.15 K	293.15 K	303.15 K	313.15 K	323.15 K	333.15 K	343.15 K	353.15 K
$(\Delta c/\Delta P)_S/10^{-6} \text{ m}^2 \text{ s kg}^{-1}$								
6	6.50	6.93	7.38	7.92	8.43	9.04		
7	6.13	6.47	6.84	7.33	7.83	8.34	8.87	
8	5.82	6.14	6.50	6.90	7.29	7.69	8.17	8.62
9	5.61	5.94	6.25	6.58	6.90	7.26	7.66	8.09
10	5.46	5.69	5.97	6.27	6.59	6.95	7.32	7.70
11	5.32	5.60	5.86	6.13	6.42	6.72	7.05	7.41
12	5.16	5.41	5.68	5.98	6.26	6.57	6.91	7.29
13	5.07	5.30	5.57	5.88	6.14	6.41	6.73	7.06
<i>B/A</i>								
6	9.94	10.05	10.12	10.25	10.27	10.34		
7	10.15	10.20	10.25	10.43	10.56	10.64	10.68	
8	10.22	10.29	10.39	10.52	10.58	10.61	10.70	10.70
9	10.32	10.46	10.53	10.60	10.61	10.65	10.70	10.76
10	10.43	10.42	10.48	10.55	10.61	10.69	10.75	10.79
11	10.48	10.60	10.65	10.69	10.73	10.75	10.79	10.84
12	10.44	10.52	10.62	10.73	10.79	10.86	10.94	11.06
13	10.49	10.55	10.66	10.82	10.86	10.88	10.97	11.04
$\delta\phi/10^{-12} \text{ s}^3 \text{ kg}^{-1}$								
6	4.96	5.74	6.64	7.78	9.06	10.68		
7	4.28	4.87	5.56	6.44	7.46	8.63	10.01	
8	3.81	4.32	4.90	5.60	6.37	7.25	8.33	9.53
9	3.49	3.95	4.44	5.00	5.63	6.36	7.22	8.22
10	3.26	3.61	4.04	4.53	5.09	5.75	6.49	7.33
11	3.06	3.43	3.81	4.24	4.74	5.30	5.95	6.70
12	2.88	3.21	3.58	4.00	4.46	4.98	5.59	6.30
13	2.76	3.06	3.41	3.82	4.24	4.71	5.26	5.87

with either temperature or carbon number are illustrated in Figure 1. The pressure derivative of sound speed $(\Delta c/\Delta P)_S$ increases regularly and rapidly with temperature. A relative change of 40% in the value of the pressure derivative of sound speed $(\Delta c/\Delta P)_S$ is observed when temperature is changed from 283.15 to 333.15 K. The sound speed derivatives of pressure $(\Delta c/\Delta P)_S$ decrease monotonously with the increase of the number of $-\text{CH}_2$ group as shown in Figure 1 which reveals a significant influence of the chain length on the pressure derivative of sound speed. This phenomenon is in accordance with the results of Sarvazyan *et al.*, in their studies on aqueous solutions of amino acids and proteins [6].

The B/A parameters for the same substances were deduced (Tab. I) by combining these experimental data with the density values of Rossini [17] and with speed of sound data taken from the literature [18–20]. As shown in Figure 2, values increase slightly with temperature. The maximum temperature coefficient is equal to 0.01/K for C_7 and the minimum temperature coefficient is equal to 0.005/K for C_{11} . These relatively small temperature coefficients indicate that the B/A parameter of linear alkanes is not very sensitive to temperature. In the case of C_7 in which the maximum temperature coefficient was observed, the variation of B/A is only 5% of the B/A value

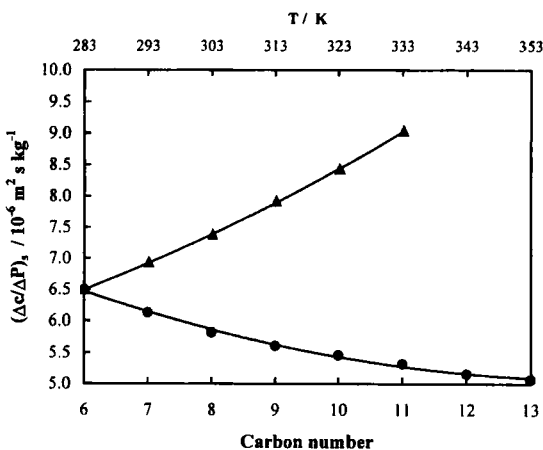


FIGURE 1 -▲-, Pressure derivative of sound speed of $n\text{-C}_6$ as a function of temperature. -●-, Pressure derivative of sound speed of normal alkanes as a function of carbon number at $T = 283.15 \text{ K}$.

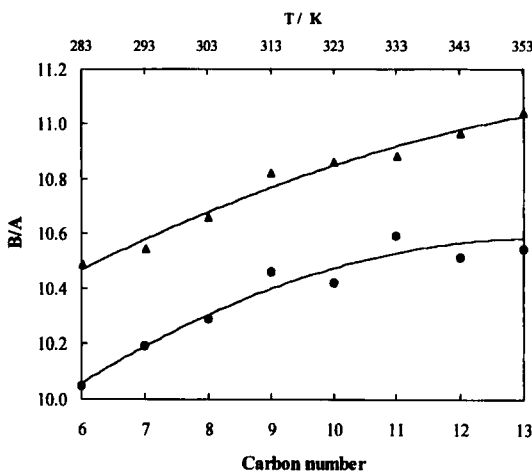


FIGURE 2 -▲-, acoustic nonlinearity parameter B/A of C_{13} as a function of temperature. -●-, acoustic nonlinearity parameter B/A of normal alkanes as a function of chain length at $T=293.15$ K.

when temperature is changed from 283.15 to 343.15 K. The result that B/A is insensitive to temperature is consistent with that of other B/A investigations [5, 21–22].

As can be seen from Table I and Figure 2, the B/A values increase of about 1.5% with the increase of a $-\text{CH}_2-$ group around the C_7 , whereas when the carbon number increases further, the rate of the augment of B/A decreases. For the case of C_{11} , C_{12} , C_{13} , for example, there is even no obvious difference of B/A between each other. Thus, due to the compensation of two separate effects (*i.e.*, the increase of the density and the sound speed whereas the $(\Delta c/\Delta P)_S$ coefficient decrease as a function of the carbon number), the variation of the B/A parameter with the chain length is less significant than the experimental uncertainty. In order to avoid the deficiency, it is convenient to introduce a new parameter, called the phase shift parameter $\delta\phi$ defined as:

$$\delta\phi = \frac{B/A}{2\rho c^3} \quad (8)$$

The values of the phase shift parameter of linear alkanes are listed in Table I and illustrated in Figures 3 and 4 as a function of temperature and as a function of carbon number respectively. Like the pressure

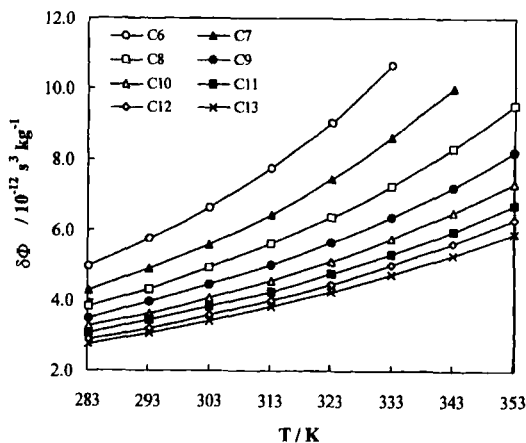


FIGURE 3 The phase shift parameter of linear alkanes as a function of temperature.

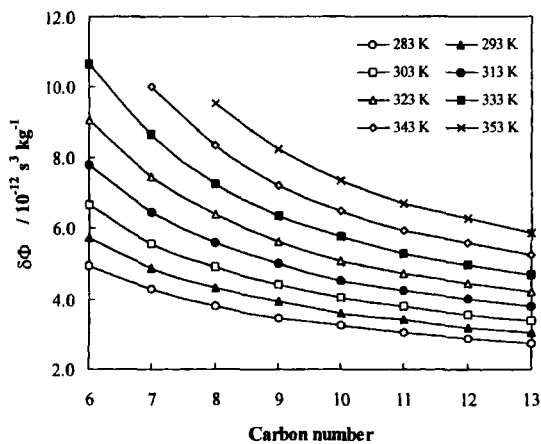


FIGURE 4 The phase shift parameter of linear alkanes as a function of molecular weight at various temperatures.

derivative of sound speed $(\Delta c/\Delta P)_S$, the phase shift parameter increases rapidly with temperature. The rate of increase is even faster than that of the pressure derivative of sound speed $(\Delta c/\Delta P)_S$, as shown in Figure 3. The phase shift parameter also shows (Fig. 4) a more rapidly decreasing trend with the addition of carbon chains, or $-\text{CH}_2$ groups than that of $(\Delta c/\Delta P)_S$, and reveals a significant influence of the change of molecular structure.

It should be pointed out that the phase shift parameter can be measured directly by the phase comparison method, without the knowledge of density and sound speed of the material studied, because it can be seen from Eq. (4) that this property parameter can be expressed as follows:

$$\frac{(B/A)}{2\rho c^3} = -\frac{1}{\omega d} \left(\frac{\Delta\phi}{\Delta P} \right)_S \quad (9)$$

For our measurement system, the distance between the two transducers d and the frequency of signal are constants. So, interest focuses on the changeable term, *i.e.*, the $(\Delta\phi/\Delta P)_S$, where $\Delta\phi$ is the phase shift caused by the change of pressure; that is why the term $(B/A)/2\rho c^3$ is called the phase shift parameter.

The fact that, as we described above, this parameter is more sensitive to the temperature and to the change of molecular structure than B/A and the pressure derivative of sound speed $(\Delta c/\Delta P)_S$ and can be measured directly by the phase comparison method, means that it can become a new parameter like other parameters such as density, sound speed, attenuation, impedance, and the acoustic non-linearity parameter B/A to characterize the fluids and further be used in medical imaging applications. In fact, several authors have already applied this parameter in their studies [6, 8, 23–27]. The difference is that they merely treated the term $(B/A)/2\rho c^3$ or other similar forms in their articles as a physical quantity that contained B/A and did not regard the phase shift parameter as an individual variable.

The phase shift parameter has another advantage over the acoustic nonlinearity parameter B/A . It is an independent parameter whereas the B/A , as demonstrated by some authors [28–30], is not completely independent. There is mathematical correlation between B/A and sound speed. Besides, from its definition, one can immediately observe that B/A depends on density and sound speed. This will pose a problem when it is applied to B/A imaging where the density and impedance have to be assumed to be constant. From this point of view, the phase shift parameter is a more physical quantity than B/A , which can reveal some distinctive

physical feature of fluids and give a higher resolution rate in medical imaging.

4. THE MEASUREMENT FOR ISOMERS

To further demonstrate the idea above, a study was carried out for four isomers: hexane, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane. They are known to have the same chemical formula C_6H_{14} but different molecular structures.

The pressure derivative of sound speed, the acoustic nonlinearity parameter B/A , as well as the phase shift parameter of these compounds are displayed in Table II and illustrated in Figures 5 to 7.

Figure 6 shows that, although these four isomers have similar molecular structure, their B/A behaviours are slightly different. Negative temperature coefficients were observed for 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane except hexane. The appearance of a negative temperature coefficient is not a strange phenomenon. In fact, some researchers have reported that the B/A values decreased with temperature for benzene [21]. For us, the thing of interest is that the phase shift parameter (see Fig. 7) of the isomers also

TABLE II Pressure derivative of sound speed and related parameters for various isomers of hexane

<i>Isomers</i>	283.15 K	293.15 K	303.15 K	313.15 K	323.15 K
$(\Delta c/\Delta P)_s/10^{-6} m^2 s kg^{-1}$					
Hexane	6.50	6.93	7.38	7.92	8.43
2-methylpentane	6.86	7.26	7.63	8.05	8.51
3-methylpentane	6.84	7.18	7.58	8.00	
2,3-dimethylbutane	6.69	7.07	7.55	7.92	
<i>B/A</i>					
Hexane	9.94	10.05	10.12	10.25	10.27
2-methylpentane	10.11	10.10	10.01	9.95	9.88
3-methylpentane	10.52	10.44	10.41	10.36	
2,3-dimethylbutane	10.03	10.01	10.09	9.97	
$\delta\phi/10^{-12} s^3 kg^{-1}$					
Hexane	4.96	5.74	6.64	7.78	9.06
2-methylpentane	5.54	6.39	7.34	8.50	9.88
3-methylpentane	5.24	5.99	6.89	7.95	
2,3-dimethylbutane	5.35	6.16	7.19	8.26	

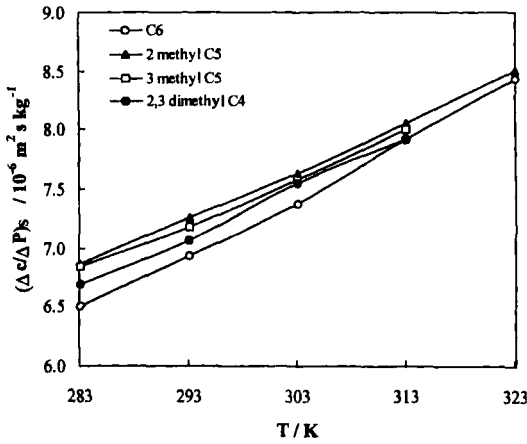


FIGURE 5 Pressure derivative of sound speed of various isomers of hexane as a function of temperature.

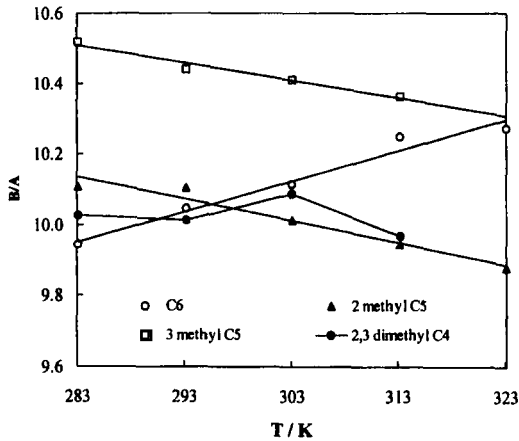


FIGURE 6 Acoustic nonlinearity parameter B/A of various isomers of hexane as a function of temperature.

displays the distinctive difference between them; the four curves are separated clearly and there are no intersections unlike. The significant influence of molecular structure and temperature on the phase shift parameter has been revealed for these four isomers. Therefore, the phase shift parameter is further proved to be a promising parameter for the investigation of fluids.

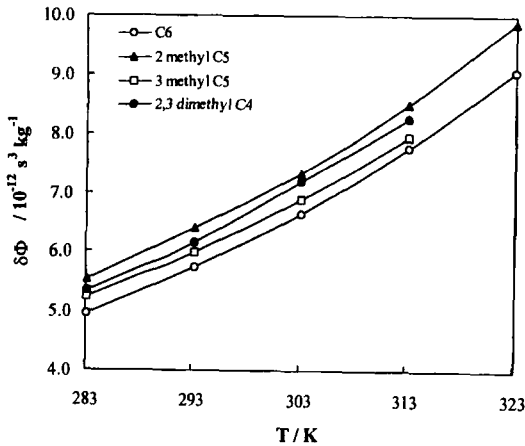


FIGURE 7 The phase shift parameter of various isomers of hexane as a function of temperature.

5. CONCLUSION

The study of linear alkanes and isomers by using the acoustic nonlinearity parameter B/A and the phase shift parameter, as described above, yields interesting results. Particularly, it is revealed that the phase shift parameter is more sensitive to temperature and molecular structure than B/A and the pressure derivative of sound speed. This feature of the phase shift parameter, along with other advantages over B/A such as its easy measurability and relative independence, means that it can be used as a promising parameter for the characterization of fluids and application in medical imaging.

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