Molecular structure dependence of acoustic nonlinearity parameter B/A for silicone oils*

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Exploring new acoustic parameters is essential to develop a noninvasive imaging technique for the surgery of silicone oil tamponades. In this study, the acoustic nonlinearity parameters B/A of varied silicone oil samples (e.g., linear or hyper-branched) are experimentally measured by using a modified thermodynamic method. The results show that: (i) when the concentration of the silicone oil with a molecular weight of 5×10^4 increases from 0.5 g/100 ml to 8 g/100 ml, the corresponding B/A value increases by about 18%, but the acoustic velocity only increases by about 0.1%; (ii) when the molecular weight of the hyper-branched silicone oil is enhanced from 2×10^5 to 1×10^6, the B/A value increases by about 22%, while the acoustic velocity is only raised by about 0.2%. This study suggests that the B/A parameter of the silicone oil is more sensitive to the change in its molecular structure than that of the acoustic velocity. Thus, the B/A parameter might be utilized as an effective index for the development and optimization of the noninvasive imaging of the surgery of silicone oil tamponades.

Keywords: acoustic nonlinearity parameter, molecular structure, modified thermodynamic method, silicone oil

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1. Introduction

Retinal detachment (RD) is one of the most common diseases in the posterior segment of the eye. It occurs when the neural retina detaches from the choroid, resulting in the eventual death of the retina and partial or complete loss of vision. Since the first use of silicone oil as an ocular tamponade agent in clinical retinal therapy,[1] silicone oil has been widely used to treat complicated retinal detachments.[2] Silicone oils are generally polydispersed synthetic polymers consisting of mixtures of linear and cyclic species with different sizes of molecular chains. Though the silicone oil is stable in tissues, it might cause glaucoma or cataract development. As a result, it is required to develop a precise biometry for the surgery of silicone oil tamponades. Biometry based on acoustic velocity can be performed to measure the axial length (AL) in silicone oil-filled eyes.[3,4] The newly developed ultrasonic bio-microscopy can image the changes in the silicone oil-filled eyes, and predict the danger of recurrent retinal detachment.[5] However, the sensitivity of acoustic velocity to the structure change is not high enough. Recently, researchers proposed an optical measurement modality with higher sensitivity, but the optical device is complicated and of a high price.[6] Therefore, there is an urgent demand for exploring new ultrasonic parameters with high sensitivity for the development of the noninvasive ultrasonic imaging modality used in the surgery of silicone oil tamponades.

Moreover, it has been proven that many anomalies in a medium can be detected by using the acoustic nonlinearity. The acoustic nonlinearity parameter B/A could provide significant structure information of a medium.[7,8] Studies on the B/A parameters of aqueous solutions of organic and inorganic compounds suggest that it is dependent on the chemical composition of solutions and the molecular structure of the solutes.[9,10] Furthermore, the B/A parameter is more sensitive to the pathological status of tissues than the linear parameters such as acoustic velocity.[11,12] Therefore, B/A might be used as an effective parameter for the ultrasonic tissue characterization.

The aim of this study is to examine the possibility of using the B/A parameter to detect the structure change of silicone oil. For this purpose, an automatic experimental system is developed to measure the B/A of silicone oil samples with two different structures (i.e., linear and hyper-branched), based on the modified thermodynamic method. The molecular structure dependences of the B/A parameter and the acoustic velocity of the hyper-branched silicone oil samples are discussed in detail.

2. Acoustic nonlinearity parameter and modified thermodynamic method

For thermoviscous fluids, the Taylor expansion of the relation between pressure and density for an adiabatic process

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is[7]

$$p = p_0 + \left(\frac{\partial p}{\partial \rho}\right)_{S,\rho=\rho_0} (\rho - \rho_0) + \frac{1}{2}\left(\frac{\partial^2 p}{\partial \rho^2}\right)_{S,\rho=\rho_0} (\rho - \rho_0)^2 + \frac{1}{3!}\left(\frac{\partial^3 p}{\partial \rho^3}\right)_{S,\rho=\rho_0} (\rho - \rho_0)^3 + \cdots, \quad (1)$$

where p and ρ represent the instantaneous pressure and density; p_0 and ρ_0 are the equilibrium values of the pressure and density; S is the entropy of the fluid. Equation (1) can be equivalently rewritten by means of A, B, and C as

$$p = p_0 + A\left(\frac{\rho - \rho_0}{\rho_0}\right) + \frac{1}{2}B\left(\frac{\rho - \rho_0}{\rho_0}\right)^2 + \frac{1}{3!}C\left(\frac{\rho - \rho_0}{\rho_0}\right)^3 + \cdots, \quad (2)$$

with

$$A = \rho_0 \left(\frac{\partial p}{\partial \rho}\right)_{S,\rho=\rho_0} = \rho_0 c_0^2,$$

$$B = \rho_0^2 \left(\frac{\partial^2 p}{\partial \rho^2}\right)_{S,\rho=\rho_0},$$

$$C = \rho_0^3 \left(\frac{\partial^2 p}{\partial \rho^2}\right)_{S,\rho=\rho_0},$$

where c_0 is the infinitesimal ultrasonic wave velocity. It should be noted that the term C is negligible for a Mach number lower than 10^{-4}. The acoustic nonlinearity parameter B/A is defined as the ratio of the quadratic terms to the linear terms of the Taylor series expansion[7]

$$B/A = 2\rho_0 c_0 \left(\frac{\partial c}{\partial p}\right)_{s,\rho=\rho_0}, \quad (3)$$

with $c^2 = (\partial p/\partial \rho)_S$. Therefore, the B/A parameter is directly related to the change in the ultrasonic velocity with an isentropic change of the static pressure.

Two methods are usually used to measure the acoustic nonlinearity parameter B/A, i.e., the finite amplitude method and the thermodynamic method. The former measures the waveform distortion owing to the generation of harmonics during the sound propagation, while the latter is based on the expression[7]

$$B/A = 2\rho_0 c_0 \left(\frac{\partial c}{\partial p}\right)_T + \frac{2c_0 T\eta}{C_p}\left(\frac{\partial c}{\partial T}\right)_p,$$

where T is the absolute temperature, η is the volume coefficient of thermal expansion, C_p is the specific heat capacity, and $(\partial c/\partial p)_T$ and $(\partial c/\partial T)_p$ are the change of the sound velocity with pressure at constant temperature and the change of sound velocity with temperature at constant pressure, respectively. The accuracy of the finite amplitude method is less than that of the thermodynamic method, because its accuracy is affected by the calibration of the transducers and the sound diffraction. However, the experimental setup for the thermodynamic method is complicated due to the requirement of large pressure change (1–100 atm). In this study, the B/A measurement is performed based on a modified thermodynamic method with a simplified experimental system.[13] The main point of this method is to make direct isentropic measurements of sound-speed variation rather than using an isothermal process.[13]

As shown in Fig. 1, the signal U_1 (the reference signal) generated from the signal generator is used to drive the transmitter. U_2 is the signal detected by the receiver, and d represents the distance between the transmitter and the receiver. Both U_1 and U_2 are sent to a phase detector, which is used to detect the phase shift. U_1 and U_2 can be written as

$$U_1 = A_{10}\sin(\omega t + \phi_{10}), \quad (4)$$

$$U_2 = A_{20}\sin[\omega(t - d/c) + \phi_{20}], \quad (5)$$

where A_{10} and A_{20} are the amplitudes of the reference signal and the detected signal, ω is the angular frequency, and ϕ_{10} and ϕ_{20} are the initial phases of the two signals.

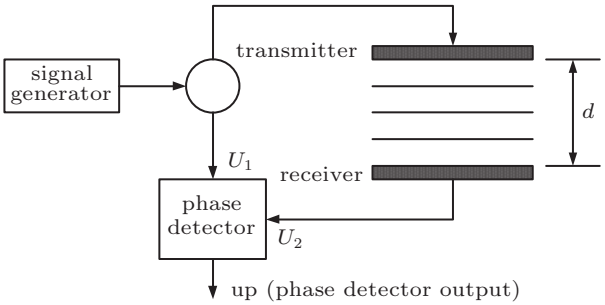


Fig. 1. Illustration of the phase shift detecting.

The output of the phase detector is

$$U_p = kA_{10}A_{20}\sin(\omega d/c + \phi_{10} - \phi_{20} + \pi/2), \quad (6)$$

where k is a constant that depends on the property of the phase detector. Assuming that $\phi = \omega d/c + \phi_{10} - \phi_{20} + \pi/2$, equation (6) can be rewritten as

$$U_p = kA_{10}A_{20}\sin\phi. \quad (7)$$

In this method, the distance between the transmitter and the receiver should be initially adjusted to satisfy the null condition, i.e., $\phi = n\pi$. Under this null condition, the phase change will take a low value. If the distance between the two transducers, the transmitting frequency and the initial phases are fixed, and a variation of the phase shift $\Delta\phi$ is given by

$$\Delta\phi = -\omega d\Delta c/c^2. \quad (8)$$

The corresponding output of the phase detector is

$$\Delta U_p = kA_{10}A_{20}\Delta\phi. \quad (9)$$

By inserting Eq. (8) into Eq. (3), we can obtain

$$\frac{B}{A} = -\frac{2\rho c^3}{\omega d}\frac{\Delta\phi}{\Delta P}. \tag{10}$$

By combining Eqs. (8) and (9), the B/A parameter can be written as

$$\frac{B}{A} = -\frac{2\rho c^3}{\omega d k A_{10} A_{20}}\left(\frac{\Delta U_{\mathrm{P}}}{\Delta P}\right)_{\mathrm{s}}. \tag{11}$$

Therefore, the measurement of the B/A parameter can be determined by measuring the phase change caused by an isentropic static pressure change. In order to approximate the isentropic condition, the time for the measurement is required to be about 1–2 s, and the pressure change should be around 1–2 atm.[13]

3. Experimental setup and sample preparation

Figure 2 illustrates the experimental setup for measuring the B/A parameter by using the modified thermodynamic method. A function generator (Agilent 33250A, USA) is used to produce a 5-MHz sinusoidal signal that is sent to a mixer (ZAD-8, Mini-Circuits, USA). Another function generator (Agilent 33250A, USA) is used to generate a gate signal to control the output signals of the mixer, which are 5-MHz tone bursts with a duration of 15 μs and a pulse repetition frequency of 2.2 kHz. These tone bursts are amplified by using a power amplifier (ENI2100L, USA) to drive a planar transmitter (with a center frequency of 5 MHz). The transmitter and the receiver are located at the two ends of the measurement cell, the distance between which should satisfy the null condition. The amplitudes of the output signals are kept unchanged during the measurements by using an attenuator and a pre-amplifier. The second double balanced mixer (ZAD-8, Mini-Circuits, USA) is used to detect the phase shift between the reference signal and the output of the receiver. The nonlinear components in the detected phase signal and the high frequency noise generated by the measurement apparatus are filtered by a low-pass filter with a cut-off frequency of 300 kHz. A digital oscilloscope (Agilent 54830, USA) is used to capture the signal waveforms necessary for the B/A measurements. A digital sampling card (PCI-9812, ADLink, USA) is used to record the dc output voltage. All the data acquisition devices (e.g., function generators, sampling card, and signal processing) are controlled by a microcomputer via the GPIB interface and the LabView software.

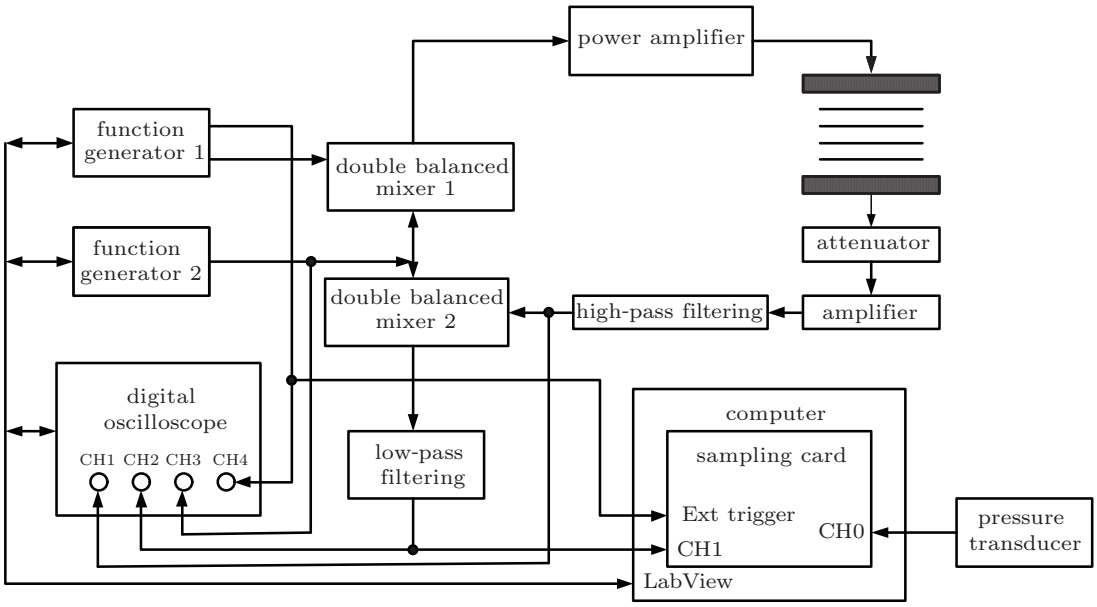


Fig. 2. Experimental setup for measuring B/A by using the modified thermodynamic method.

To investigate the molecular structure dependence of the B/A parameter, two kinds of silicone oils with different structures (i.e., linear and hyper-branched) are used in this study. The traditional linear silicone oil with a number-average molecular weight of 5×10^4 is prepared according to Ref. [14]. The hyper-branched silicone oil is prepared according to the following steps:[15] (i) 0.01%–59.90% tetramethylammonium hydroxide polydehral oligomer silsesquixane (POSS), 16.90%–99.99% oligomeric polydimethylsiloxanols (D3, D4, or DMC), and 0–65.50% blocking agent are mixed; (ii) the mixture is stirred at the temperature 20–130 °C under nitrogen atmosphere, and the reaction is kept for about 10 min to 48 hour; (iii) to obtain the hyper-branched silicone oil, the reaction temperature is then heated to 135–200 °C,

and the tetramethylammonium hydroxide is removed; and (iv) the hyper-branched silicone oils with a molecular weight from 2×10^5 to 10×10^5 are eventually synthesized. The molecular weights of hyper-branched silicone oils could be controlled by adjusting the ratio of the mixture in the first step. For example, the hyper-branched silicone oil with a molecular weight of $8 \times 10^5$is synthesized with the mixture of 0.14% tetramethylammonium hydroxide POSS, 99.67% D4, and 0.19% block agent.

In the measurements, the silicone oil samples are filled in the measurement cell immersed in a water tank at a temperature of 25 °C. The static pressure change is controlled by opening or closing the valves, and measured by using a sensor (HBM, model P3MB-100 MPa). As long as the switch of the valve is fast enough (between 1–2 s) and the pressure variation is weak (about 1 atm), the pressure change could be regarded as isentropic. In all the studies, six repetitive measurements are performed for each sample, and the measured data are represented by the mean values and standard deviations.

4. Results and discussion

First of all, the B/A parameters and the acoustic velocities for the linear and hyper-branched silicone oil samples are measured and compared. Various quantities of the linear silicone (molecular weight is 5×10^4) and the hyper-branched silicone oil (molecular weight is 5×10^5) are dissolved in the methylbenzene, so that the silicone oil samples with various concentrations are derived for the measurements. Figure 3 shows the measured B/A for the linear and hyper-branched silicone oil samples as functions of the concentration. At the initial concentration (0.5 g/100 ml), the B/A for the hyper-branched silicone oil is about 9.53, which is about 12% larger than that of the linear branched silicone oil (8.50). However, the acoustic velocity of the hyper-branched silicone oil (1359.2 m/s) is only 0.1% larger than that of the linear silicone oil (1357.8 m/s). As the concentration increases, both the B/A parameters and the acoustic velocities for the linear and hyper-branched silicone oil show a linear increasing tendency. When the concentration reaches 8 g/100 ml, the B/A and the acoustic velocity for the hyper-branched silicone are 11.3 and 1361.2 m/s, respectively; while the corresponding values for the linear silicone oil are 9.4 and 1359.5 m/s. The linearity of these dependences indicates that the B/A parameter of the solution is not sensitive to solute–solute interactions, and that only solute–solvent interactions contribute to the B/A increment. In addition, the results indicate that: (i) the hyper-branched silicone oil shows larger nonlinearity than the linear silicone oil owing to a more complicated structure; and (ii) the B/A parameter is more sensitive to the variation of the concentration than the acoustic velocity. For example, as the concentration rises from 0.5 g/100 ml to 8 g/100 ml, the B/A parameter for the hyper-branched silicone oil increases by about 18%, while the acoustic velocity only increases by 0.1%.

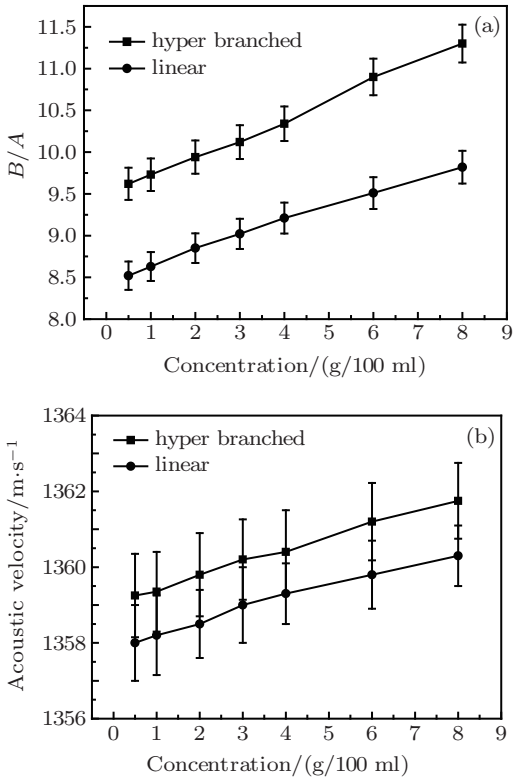


Fig. 3. Acoustic nonlinearity parameter and acoustic velocity as functions of the concentration of the silicone oil samples. (a) B/A; (b) acoustic velocity.

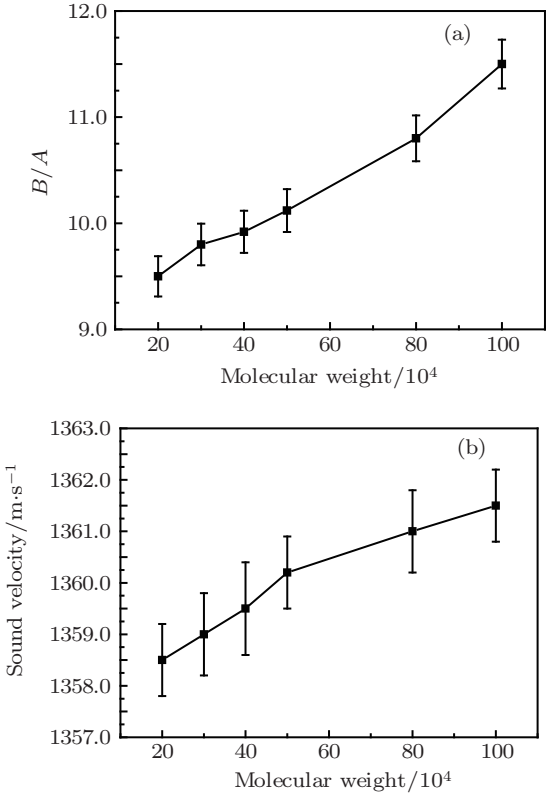


Fig. 4. Molecular weight dependences of (a) the acoustic nonlinearity parameter and (b) acoustic velocity.

Secondly, the molecular weight dependences of the B/A parameter and acoustic velocity for the hyper-branched silicone oil are studied. The molecular weight ranges from 2×10^5 to 1×10^6. Figure 4 plots the molecular weight dependences of the B/A parameter and the acoustic velocity for the hyper-branched silicone oil. As the molecular weight increases, both the B/A parameter and the acoustic velocity are almost linearly enhanced. When the molecular weight increases from 2×10^5 to 1×10^6, the acoustic velocity only increases by 0.2% (from 1358.4 m/s to 1361.3 m/s); while the B/A parameter shows a 22% increment (from 9.4 to 11.5).

The chemical structure of the conventional linear-branched molecular silicone oil is shown in Fig. 5(a), where methyl R_1 and R_2 along the chain can be substituted by many other groups (e.g., phenyl, vinyl, or trifluoropropyl). The Si–O bonds are strongly polarized and without protection, which could lead to strong intermolecular interactions. However, the methyl groups, only weakly interacting with each other, shield the main chain. As a result, chain-to-chain interactions are weak, and the distance between adjacent chains is relatively large in silicones. Owing to the weak intermolecular interactions, the linear silicones would have a brittle structure. By contrast, by use of the POSS (as shown in Fig. 5(b)), branched molecules with molecular weights higher than 10^5 could be generated. Therefore, the hyper-branched silicones would exhibit better thermal and mechanic properties.

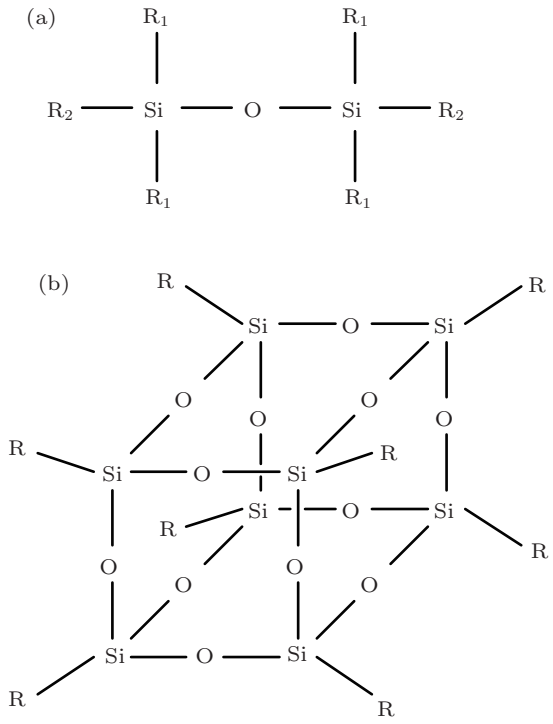


Fig. 5. Molecular structures of (a) linear and (b) hyper-branched silicone oils.

The acoustic velocity in the liquid can be expressed as: $c^2 = 1/(\beta\rho)$, where ρ is the density, and β is the isentropic coefficient of compressibility. The enhanced intermolecular interaction could raise the value of β, leading to the increase in the acoustic velocity. The value of the B/A parameter is affected by not only the physical parameters (such as the density, acoustic velocity, isentropic coefficient of compressibility, and so on), but also the molecular structure. Zhang *et al.* indicated that the B/A parameter for biological tissues depends on three levels of biological structure, i.e., the tissue level, the cellular level, and the molecular level.[16] Sarvazyan *et al.* proved that strong intermolecular solute–solvent interactions, such as electrostriction in the hydration shell of charged atomic groups or hydrogen bonding in the hydration shell of polar groups, lead to an increase in the B/A parameter of the solution.[17] Considering the complicated chain structure of aqueous solutions, Flory *et al.* indicated that the B/A parameter should be mainly determined by the ratio of molecular core volume to the total volume.[18] Owing to the enhancement of the intermolecular interaction, this ratio has a significant change for the hyper-branched silicone, which should lead to an increase in the B/A value.

The uncertainty of the B/A parameter can be evaluated from the summation of errors resulting from each term in Eq. (11). The major source of uncertainty in this equation is the result of the experimental assessment of $(\Delta U_p/\Delta p)_s$, which is estimated approximately to be 0.6%. The acoustic velocity induces an inaccuracy of 0.5%. As for the density value, it will bring about an uncertainty of less than 0.5%. The term $kA_{10}A_{20}$ is assumed to be constant in the measurement and the frequency error is also negligible. According to the arithmetic sum of each uncertainty listed above, an estimate of the inaccuracy of the B/A parameter should be less than 2%.

Although the obtained results have shown the possibility of examining the molecular change of silicone oil by using the B/A parameter, further studies on the practical B/A imaging technique are still required for surgery using silicone oil tamponades. Owing to the specificity of eye surgery, it is necessary that the B/A parameter should be evaluated safely for small samples. Recently, Saito *et al.* developed a finite amplitude method for imaging the B/A parameter of a sample as small as 0.1 ml using 18.6-MHz focused ultrasound,[19,20] which might enable more opportunities of applications of the B/A imaging technique in clinic.

5. Conclusion

It is important to explore new ultrasonic parameters for the development and optimization of the noninvasive imaging technique of the surgery using silicone oil tamponades. In this study, the possibility of using the acoustic nonlinearity parameter B/A to assess the structure change of silicone oil is experimentally examined by using a modified thermodynamic

method. The results indicate that the B/A increment is contributed by a more complicated molecular structure or larger molecular weight. Furthermore, it is found that the change of B/A parameter is much more sensitive to the molecular structure change than other linear parameters such as the ultrasound velocity, which might provide valuable proof for the potential application of the B/A parameter in the noninvasive imaging of the surgery using silicone oil tamponades.

References

[1] Cibis P A, Becker B and Olcn E 1962 *Arch. Ophthalmol.* **68** 590
[2] Chen T, Ye C and Yuan Y 2012 *Chin. Phys. B* **21** 097802
[3] Siddiqui M A, Awan M A, Fairhead A and Atta H 2010 *Br. J. Ophthalmol.* **95** 142
[4] Goessler G F, Huth J K and Dietlein T S 2009 *Br. J. Ophthalmol.* **93** 1492
[5] Grigera D E, Zambrano A, Cazn G, Cavanagh E and Girado S 2000 *Retina* **20** 524
[6] Pierre–Kahn V, Quoc E B, Chauvaud D and Renard G 2005 *Invest Ophthalmol. Vis. Sci.* **46** 5543
[7] Pantea C, Ostehoudt C F and Sinha D N 2013 *Ultrasonics* **53** 1012
[8] Zhang D, Kushibiki J and Zhou W 2006 *Chin. Phys. Lett.* **23** 2807
[9] Seghal C M, Porter B R and Greenleaf J F 1986 *J. Acoust. Soc. Am.* **79** 566
[10] Apfel R E 1983 *J. Acoust. Soc. Am.* **74** 1866
[11] Gong Y J, Zhang D and Gong X F 2005 *Chin. Sci. Bull.* **50** 1975
[12] Khelladi H, Plantier F, Daridon J L and Djelouah H 2009 *Ultrasonics* **49** 668
[13] Zhu Z, Roos M S, Cobb W N and Jensen K 1983 *J. Acoust. Soc. Am.* **74** 1518
[14] Rochow E G 1987 (Berlin: Springer-Verlag)
[15] Jia X D, Ji K, He H and Ge R J 2007 CN101016384A
[16] Zhang J, Kuhlenschmidt M S and Dunn F 1991 *J. Acoust. Soc. Am.* **89** 80
[17] Sarvazyan A P and Chalikian T V 1990 *J. Acoust. Soc. Am.* **88** 1555
[18] Lu Y G and Dong Y W 2006 *Chin. Phys.* **15** 2030
[19] Saito S 2010 *J. Acoust. Soc. Am.* **127** 51
[20] Saito S and Kim J H 2011 *Rev. Sci. Instrum.* **82** 064901