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DETERMINATION OF THE NONLINEAR PARAMETER AND INTERNAL PRESSURE IN A LIQUID BY THE ACOUSTIC METHOD

Ю.М. Дудзінський, Н.В. Тітова, Н.В. Манічева, А.О. Захарова. **Визначення нелінійного параметра і внутрішнього тиску в рідині акустичним методом.** Пропонується акустичний метод оцінки молекулярних властивостей рідини, визначення нелінійного параметра рідин по співвідношенню першої і другої гармоніки при зміні акустичної хвилі, та за допомогою цього параметра вимірювання внутрішнього тиску. Також пропонований метод вимірює міжмолекулярну відстань для досліджуваних рідин. В рідинах органів посилюються ефекти розсіювання звуку та взаємодії хвиль. У рідинах організму на молекулярному рівні є незначна кількість мікроскопічних бульбашок. Це призводить до виникнення явища кавітації. Ці явища можуть бути шкідливими, але не завжди. Існують апарати біологічних і фармацевтичних технологій, медичні прилади, які успішно використовують ці ефекти. У роботі представлена функціональна схема експерименту, визначені осцилограми акустичних сигналів скінченої амплітуди на різних відстанях від випромінювача. В якості випромінювача і приймача використані однакові пристрої на основі кварцових пластин діаметром 25 мм з резонансною частотою 3 МГц. Ця різниця приблизно в три рази частот резонансу датчиків і акустичного сигналу забезпечує лінійність амплітудно-частотної характеристики обох датчиків. Нелінійні акустичні методи є світовою тенденцією у біомедичних дослідженнях, тому що відкривають нові можливості та перспективи у розробках медичних приладів. Виникнення вищих гармонік при викривленні вихідної гармонійної хвилі кінцевої амплітуди можна використовувати для експрес аналізу фізичних властивостей чистих рідин і особливо водних розчинів органічних речовин. Даний спосіб експериментального визначення нелінійного параметра і внутрішнього тиску в рідині зручніше, ніж статичний, оскільки не вимагає застосування високих надлишкових статичних тисків. Пропонований акустичний спосіб дає меншу похибку, ніж динамічний. Точність такого визначення може бути достатньою для судження про зміну міжмолекулярної взаємодії в рідинах.
Ключові слова: нелінійні хвильові ефекти, внутрішній тиск, гармоніка, акустична хвиля

Yu. Dudzinskii, N. Titova, N. Manicheva, A. Zakharova. **Determination of the nonlinear parameter and internal pressure in a liquid by the acoustic method.** An acoustic method is proposed for assessing the molecular properties of a liquid, determining the nonlinear parameter of liquids from the ratio of the first and second harmonics when the acoustic wave changes, and using this parameter to measure the internal pressure. In addition, the proposed method measures intermolecular distances for the studied liquids. In organ fluids, the effects of sound scattering and wave interaction are enhanced. In body fluids, at the molecular level, there is a small amount of microscopic bubbles. This leads to the appearance of the phenomenon of cavitation. These phenomena can be harmful, but not always. There are devices for biological and pharmaceutical technologies, medical devices that successfully use these effects. The paper presents a functional diagram of the experiment, identifies the oscillograms of acoustic signals of finite amplitude at different distances from the emitter. The same devices based on quartz plates 25 mm in diameter with a resonance frequency of 3 MHz were used as the emitter and receiver. This difference of approximately three times the resonance frequencies of the sensors and the acoustic signal ensures the linearity of the amplitude-frequency response of both sensors. Nonlinear acoustic methods are a global trend in biomedical research, as they open up new opportunities and prospects in the development of medical devices. The appearance of higher harmonics in the curvature of the initial harmonic wave of finite amplitude can be used for express analysis of the physical properties of pure liquids and especially aqueous solutions of organic substances.

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This method of experimental determination of the nonlinear parameter and internal pressure in a liquid is more convenient than the static one, since it does not require the use of high excess static pressures. The proposed acoustic method gives less error than the dynamic one. The accuracy of such a determination can be sufficient to judge the change in the intermolecular interaction in liquids.

Keywords: nonlinear wave effects, internal pressure, harmonic, acoustic wave

Introduction

It has long been believed that in the problems of propagation of elastic acoustic waves of small amplitude, the waves themselves do not affect the properties of a liquid, gaseous or solid medium. Therefore, a priori assumed that it will not affect the distribution of other waves in this medium. Hence the classical principle of superposition for acoustic waves. This state is a scientific idealization. If you increase the intensity of elastic waves (finite amplitude waves) at relatively low frequencies (up to 200 kHz) or significantly increase the frequency (~1 MHz) at relatively small amplitudes, the principle of superposition is not fulfilled. It is necessary to take into account the limitation of the amplitude of the waves, when there are a large number of nonlinear effects.

The presence of organic substances in the body fluids (amino acids, fatty acids, etc.) leads to an increase in the effects of sound scattering on sound, the interaction of waves. Air is dissolved in the blood, both at the molecular level and a small number of microscopic bubbles. This leads to a decrease in the threshold value of the intensity of the waves of finite amplitude, at which the phenomenon of cavitation occurs. These nonlinear phenomena are not always harmful. Designers have to deal with them. There are devices of biological and pharmaceutical technologies, medical devices that successfully use these effects.

It can be assumed that the occurrence of higher harmonics in the curvature of the original harmonic wave of finite amplitude can be used for rapid analysis of the physical properties of pure liquids and especially aqueous solutions of organic substances.

Analysis of literature data and problem statement

For the adiabatic process in a liquid, the Theta equation is often used:

$$\rho = P^* \left[\left(\frac{\rho}{\rho_0} \right)^n - 1 \right], \tag{1}$$

where P – excess fluid pressure; ρ – the corresponding density of the liquid, ρ_0 – density at a pressure close to atmospheric $\rho = 0$, n – empirical constants [1 – 2].

Often in acoustic works another nonlinear parameter of liquid is used instead of n [3–4]:

$$\Gamma = \frac{B}{A} = (n-1) = \frac{\rho_0}{c_0^2} \frac{\partial c^2}{\partial \rho} \Big| \rho = \rho_0 , \tag{2}$$

where c_0 – the speed of sound in an undisturbed medium under the condition $\rho = 0$. The parameter P^* is called "internal pressure". It characterizes the forces of intermolecular adhesion in a continuous medium, in our case – in a liquid. It follows from formula (1) that the exact value of the adiabatic modulus of elasticity of a liquid [2]:

$$K_{ad} = \rho \left(\frac{\partial p}{\partial \rho} \right) \Big|_8 = n(\rho + P^*). \tag{3}$$

In acoustic measurements, the sound pressure ρ is many times less than P^* [2], so you can use the formula to calculate the internal pressure:

$$P^* = \frac{K_{ad} \mid_{\rho=0}}{n} = \frac{\rho_0 c_0^2}{n}. \tag{4}$$

It should be noted that in [1] another, inaccurate relationship of pressure with a nonlinear parameter is given. The internal pressure P^* can also be determined by the static method. As is known [2], the isothermal modulus of elasticity up to the members of the second order of smallness can be represented as:

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$$K_{iz} = \rho\left(\frac{\partial p}{\partial \rho}\right)\Big|_r = \chi_1(\rho + P^*). \quad (5)$$

Let's use the thermodynamic relation:

$$\frac{K_{ad}}{K_{iz}} = \frac{C_\rho}{C_v}, \quad (6)$$

where C_ρ, C_v – heat capacities at constant pressure and volume, respectively.

The purpose and objectives of the study

The aim of the work is to develop an acoustic method for estimating the molecular properties of a liquid, determining the nonlinear parameter and the internal pressure in the liquid.

To achieve this goal it was necessary to solve the following tasks: to determine ways to use the acoustic method for rapid analysis of the physical properties of aqueous solutions of organic substances and to conduct research on an experimental setup.

Materials and methods of research

From expressions (3) and (6) it follows that up to the members of the second order of smallness, we can write:

$$P^* = P^{*\prime} \rightarrow n = \chi_1 \frac{c_\rho}{c_v}, \quad (7)$$

The assumption $P^* = P^{*\prime}$ is quite natural, because the internal pressure, as a characteristic of molecular interaction, should not depend on the nature of the thermodynamic process. Using the values of the internal pressure P^*, it is also possible to estimate the intermolecular distance in the liquid [5]:

$$r_{ef} \sim \frac{2\sigma}{P^*}, \quad (8)$$

where σ – surface tension.

It is known that the distortion of waves of finite amplitude can determine the parameter of the liquid n, which characterizes the nonlinearity of equation (1). Therefore, based on formula (7), the value of P^* is calculated. The advantage of the acoustic method for determining the internal pressure is that in this case it is not necessary to perform measurements at high hydrostatic pressures, as in static methods [1 – 2].

Dynamic methods give a significant scatter of values, even for one participant [1 – 2], [6]. One of the possible reasons is the use of tubes made of different materials, with different degrees of "sticking" to them of liquid molecules in the boundary layer. Unlike dynamic methods of measuring the value of P^*, the acoustic method gives a relatively high accuracy. The acoustic method is based on the fact that the distortion of the harmonic wave of finite amplitude depends on the nonlinear parameter *n*.

In particular, the pressure amplitude of the second harmonic ρ_2 at distances *X* less than the wave stabilization distance, at acoustic Reynolds numbers large or of the order of one, will be [1], [7]:

$$\rho_2 = \frac{n+1}{4}\left(\frac{X\omega}{\rho_0 c_0^3}\rho_1^2\right), \quad (9)$$

where ρ_1 – the amplitude of the pressure of the first harmonic at the sound source, $\omega = 2\pi f$ is the circular frequency of the signal near the emitter.

As can be seen from formula (9), to determine the parameter n requires an absolute measurement of ρ_1 and ρ_2. This leads to a large error. Therefore, absolute measurements were performed only in distilled water. In transformer oil, ethyl alcohol and aqueous NaCl solutions, the nonlinear parameter was determined relative to water.

Experimental installation and methods of research

The scheme of the experimental setup is shown in Fig. 1.

The container *1*, muffled by a layer of microporous rubber *2*, is filled with distilled water. As plugs on the surface of the water freely floating layer of balls of foam *3*. As the emitter is a quartz plate *4* at a fundamental frequency of 1.5 MHz. The test liquid or distilled water (in comparative experiments) is poured into the cuvette *5*, the dimensions of which are 50×150×200 mm. The cuvette is provided with sound-transparent windows *6* with Teflon films 0.05 mm thick. The cuvette 5 is rigidly mounted in the tank *1*. The change of the test fluid was carried out without its dismantling, because even a small shift of the cuvette can lead to additional errors in determining the internal pressure.

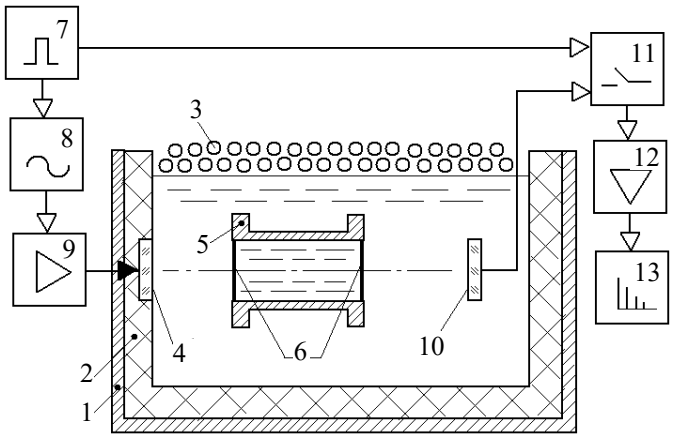

Fig. 1. Functional diagram of the experiment

The two-channel rectangular pulse generator *7*, exciting the resonant harmonic signal generator *8*, sets the duration and period of passage of the radio pulse with a frequency of 1.5 MHz. Then they come through a power amplifier to the quartz vibrator *4*, which creates an acoustic wave. Acoustic pulses after passing (with distortion) in the studied liquid medium are converted into an electrical signal by a quartz plate *10*, then through the switch *11* and the amplifier *12* are fed to the spectrum analyzer with memory *13*. From the other output of the generator *7*, a rectangular pulse with adjustable time delay is fed to the switch *11* as a control signal. The time delay corresponds to the travel time of the distance from the emitter *4* to the hydrophone *10*. The travel period is set by the pulses of the generator *7* and is selected so that the attenuated acoustic signal is almost attenuated by reflections from sound-absorbing coatings *2* and *3*. The device *7* also allows, if necessary, to put a single start of the pulse in manual mode. The spectrum analyzer *13* is equipped with a "memory" mode and stores on the screen the spectrogram of the signal until the arrival of the next pulse. Measurement of the nonlinear parameter n by the absolute levels of the first and second harmonics was performed for distilled water. Then, after replacing the liquid in the cuvette *5* was a comparison of the readings with the results for water. This took into account:

– that the boundary of two liquids separated by a Teflon film has a certain transparency coefficient *D*;

– hat part of the path between the emitter and the receiver acoustic pulse passes in the water surrounding the cuvette *5* and has a value of constant *n*, generally speaking, different from the corresponding constant of the test fluid.

We will denote the values relating to distilled water by a dash, and to another liquid by two dashes. We obtain the relationship between nonlinear parameters in the form:

$$\frac{n^n+1}{n'+1}=\left[\frac{D'}{D^n}\frac{\rho_2''}{\rho_2'}\frac{X}{L}-\frac{X}{L}+1\right]\frac{(\rho_0 c_0^3)''}{(\rho_0 c_0^3)'}\frac{D'}{D''}, \tag{10}$$

where X – the distance between the emitter and receiver, L – the length of the cuvette with the test fluid, D – the calculated transparency coefficient, the value of which for the studied liquids is in the range 0.90...0.95.

Research results

In Fig. 2 shows waveforms of acoustic signals at the output frequency of a harmonic signal of 1 MHz. As the emitter and receiver (Fig. 1) used the same devices based on quartz plates with a diameter of 25 mm with a resonant frequency of 3 MHz. This difference (approximately three times) of the resonance frequencies of the sensors and the acoustic signal provides the linearity of the amplitude-frequency characteristics of both sensors [8].

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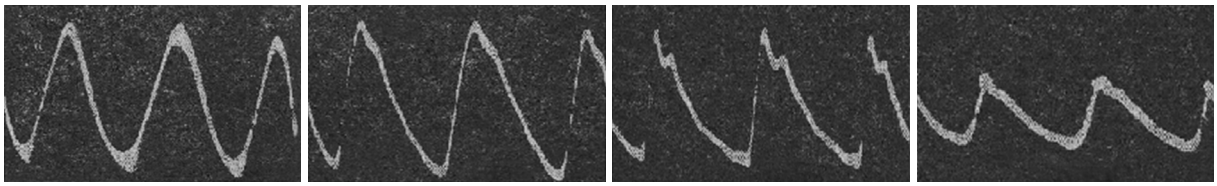

a *b* *c* *d*

Fig. 2. Oscillograms of acoustic signals of finite amplitude of frequency 1MHz at distances from the emitter: 13 wavelengths (*a)*; 67 wavelengths (*b)*; 135 wavelengths (*c)*; 320 wavelengths (*d)*

As can be seen in the oscillograms, with increasing distance between the emitter and receiver (in wavelengths), the degree of distortion of the sine wave increases. At distances greater than 100 wavelengths, the signal becomes almost sawtooth. Measurement of the nonlinear parameter *n* for the studied liquids (distilled water, ethyl alcohol, transformer oil) was performed at a temperature of 20° C. The standard deviation of the results of relative measurements did not exceed ±4 %. Absolute measurements were performed in distilled water at Reynolds acoustic numbers ~0.2…0.9. The error of direct measurements consists of errors of absolute measurements of sound pressure of the first ρ_1 and the second ρ_2 harmonics and an error at definition of sound transparency of membranes 6 of a cuvette *5*. It does not exceed value 8…10 %.

It should be noted that the value of the nonlinear parameter for distilled water changes slightly on different days and after prolonged sounding. Perhaps this is due to the processes of separation of part of the air dissolved at the molecular level in the form of microbubbles, or vice versa, with the dissolution of part of the gas molecules from the bubbles in the surrounding liquid. Processing the results of numerous absolute measurements by the method of least squares gives the value $n = 7.2 \pm 0.2$ for water, which agrees well with the data of other authors [1, 2, 9].

The experimentally obtained values of the nonlinear parameter *n* for the investigated liquids and the corresponding values of the internal pressure *P** for them are given in Table 1. There are also the results of thermodynamic calculation using the experimental dependence of the ultrasound speed of small amplitude on temperature and pressure [10]. The values of the parameter *n*, determined experimentally, by the interaction of two acoustic waves or by the optical method for distortion of a harmonic wave, are also given.

Table 1

The comparison of results of measuring

Liquid medium	P^*, MPa			*n*				$r \times 10^{10}$, m
	isothermal	adiabatic		calculation		experiment		
		[2]	This work	[7]	[8]	[9]	This work	
Distilled water	319	294	314	5.8	6.0	7.6	7.2	4.6
Ethyl alcohol	98	08	98	9.0	11.3	11.0	10.8	4.4
Transformator oil	–	238	245	–	–	7.35	7.5	4.3

The internal pressure obtained by the proposed acoustic method coincides within the measurement error with the values obtained from static measurements of the nonlinear parameter [2], with subsequent calculations by formula (6).

Table 1 shows estimates of intermolecular distance for the studied fluids on the basis of experimental data P^* and calculation by formula (5).

Fig. 3 shows the dependence of the internal pressure P^* in aqueous NaCl solutions on the salt concentration. To remove from the solution of air trapped in the dissolution of the salt, the solution was evacuated. The reason for the increase in the average internal pressure in the aqueous solution with increasing concentration of sodium chloride may be the formation around the ions of Na^+ hydrate shells with high internal pressure.

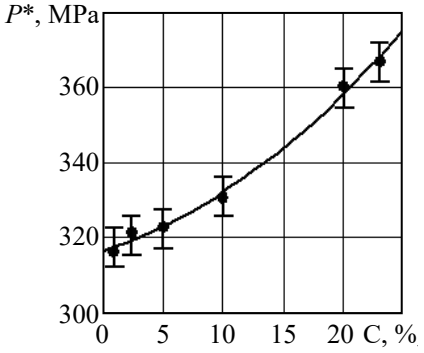

Fig. 3. Dependence of internal pressure on the concentration of NaCl solution

Conclusions

Nonlinear acoustic methods are a global trend in biomedical research, because they open new opportunities and prospects in the development of medical devices.

Occurrence of higher harmonics at curvature of the initial harmonic wave of final amplitude can be used for the express analysis of physical properties of pure liquids and especially aqueous solutions of organic substances.

This method of experimental determination of the nonlinear parameter and the internal pressure in the fluid is more convenient than static, because it does not require the use of high excess static pressures. The proposed acoustic method gives less error than the dynamic one.

In contrast to the method of estimating the intermolecular distance by the speed of ultrasound, this acoustic method allows you to directly obtain this value, assuming the applicability of the Theta equation for a particular liquid.

The accuracy of such a determination may be sufficient to judge the change in intermolecular interaction in liquids (as, for example, in the case of NaCl solutions).

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