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On the interpretation of shear viscosity ultrasonic measurements

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ABSTRACT

This article discusses the possibility of using the measurements of ultrasonic wave parameters to estimate numerical values of shear and bulk viscosities on-line. It is noted that to increase the reliability of such estimates, it is necessary to introduce classification criteria for liquids. The on-line classification of liquids can be carried out through the measurement and comparison of the real and imaginary parts of liquid acoustic shear impedances. When the measured real and imaginary parts of the impedance are equal, the calculated ultrasonic viscosity values do not differ from the shear viscosity measured by a capillary viscometer. This occurs in liquids with a shear viscosities of less than 0.015 … 0.02 $\text{Pa} * \text{s}$ (i.e., low-viscous liquids). If the real and imaginary components of the liquid shear impedance are not equal, however, the proportionality coefficient between the viscous tensor and the shear strain rate becomes a complex number, and the calculated shear viscosity values are significantly different from values obtained by the capillary viscometer. This holds true in viscous liquids. The interpretation of the results in viscous non-polymeric liquids is considered in detail within the framework of the Maxwell model, and also within the framework of a proposed shear viscosity relaxation model. The influence of the relaxation process on the measured values of ultrasonic shear viscosity is considered. As an example, the model takes into account the presence of small molecular clusters in viscous liquids. The propagating viscous wave breaks the equilibrium distribution of the clusters, which in turn causes the relaxation process.

It is shown that the shear viscosity of such liquids calculated from the ultrasonic data becomes a complex quantity depending on the frequency. A scheme for bulk viscosity measurements in the on-line mode is proposed. To find numerical values of the bulk viscosity, it is necessary to measure the real and imaginary components of the liquid shear impedance and the absorption coefficient of the longitudinal waves (if the thermal conductivity contribution can otherwise be neglected). Then the Stokes sound absorption coefficient and, accordingly, the numerical value of the bulk viscosity coefficient can be calculated.

1. Introduction

Measuring liquid parameters directly during their practical use and manufacturing presents the basis of modern technological process control. Ultrasonic means and methods are a useful technique in the taking of on-line liquid parameter measurements. They are based, as a rule, on the known mathematical linkage between the liquid parameters and parameters characterizing the propagation and reflection of longitudinal ultrasonic waves. If the ultrasonic wave frequency $\omega = 2\pi f$ is low in comparison with the inverse characteristic time $1/\tau_l$ of the relaxation processes occurring in the liquid to be measured, then the corresponding equations can be presented in the form [1]

$$c_l = \frac{1}{\sqrt{\beta\rho}}; \quad \alpha_l = \frac{\omega^2}{2\rho c_l^3}\left(\frac{4}{3}\eta_S + \eta_B\right); \quad R_{liq}^l = \frac{1 - Z_{liq}^l/Z_{sol}^l}{1 + Z_{liq}^l/Z_{sol}^l}. \tag{1}$$

Here c_l and α_l are the propagation velocity and the absorption coefficient of the longitudinal wave, R_{liq}^l is the longitudinal wave reflection coefficient at the boundary of two mediums (as a rule solid-liquid); ρ, β, η_S and η_B are the density, compressibility, shear and volume (second) viscosities of liquids; and Z_{sol}^l and Z_{liq}^l are the longitudinal wave acoustic impedances of a solid and liquid. The experimentally determined quantities are the propagation velocity, the attenuation coefficient of longitudinal waves and their reflection coefficient.

The measurements of a liquid's density and compressibility based on joint measurements of the longitudinal wave velocity and the reflection coefficient have been carry out by many authors.

The frequency dependencies of longitudinal wave attenuation coefficient and their applications for the bulk viscosity estimation of liquids were also investigated in detail.

However, it is easy to see that to find the numerical values of both viscosities, the system of equations above (1) must be supplemented. As a rule, the necessary numerical values of shear viscosity η_S are found by means of independent non-ultrasonic methods. Following which, the

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bulk viscosity η_B is computed from the difference α^r between the measured absorption coefficient α_l and the calculated so-called Stokes ultrasonic absorption coefficient α_l^{St}, caused only by shear viscosity [1]. Usually, the numerical value of shear viscosity η_S that is used in (1) is accepted as being equal to the valueη_0 measured by the capillary (rotation) method:

$$\alpha_l^r = \alpha_l - \alpha_l^{St}; \quad \alpha_l^{St} = \frac{2\omega^2\eta_0}{3\rho c_l^3}. \tag{2}$$

However, the need to combine ultrasonic measurements c_l and α_l with capillary (rotation) measurements of shear viscosity leads to significant complications in the equipment needed for automatic measurements of liquid parameters. Therefore, as an alternative approach, ultrasonic methods for shear viscosity measurements are of interest, since they have undoubted advantages when automatic measurements are required.

It is important to note that the shear viscosity values η_0 obtained by capillary viscometers are considered as reference values in practically all standards established for various technical applications. Therefore, the viscosity value η_{us} obtained by ultrasonic methods has to always be compared to the viscosity value η_0.

It is known that ultrasonic shear viscosity measurements consist of the creation of harmonic tangential mechanical stresses on the surface of the liquid to be measured and the observation of the liquid's reaction to this excitation. As a result, a perturbation depending harmoniously on time arises near of the surface and propagates down. Although the amplitude of these ultrasonic perturbation decreases rapidly with increasing distance (as so-called viscous waves), their amplitude and propagation velocity can be observed and measured.

All methods used for these purposes measure the change in the parameters of elastic waves propagating in a solid and creating shear deformation between the solid and liquid phases, which causes the viscous waves. One of the most widely used methods is the measurement of the bulk shear wave reflection coefficient R_{liq}^s at the interface between the solid and liquid [2–7].

The second widely applicable method uses the excitation and reception of guided waves in a solid with a simple geometric form. The change in the attenuation coefficient α_W is measured when such a waveguide is in the air, and then is immersed in the liquid being investigated (usually a rod [8–17] or plate [18] is used). Since the measured parameters R_{liq}^s and α_W can be expressed in terms of shear viscosity, they are used to compute it. The most important parameter characterizing the efficiency of the viscous wave excitation by the tangential stress applied to the surface of a liquid is its shear acoustical liquid impedance Z_{liq}^S (SALI). This can be calculated and compared with an experiment the most simply and consistently (see below). In addition, there is a mathematical relationship between the Z_{liq}^S and the propagation parameters of the normal wave as well.

As shown by numerous experiments [2–18], all of the liquids studied can be divided into two groups by comparing η_{us} calculated from the ultrasonic results to the values η_0 measured by the capillary method. In the first group, the values of η_{us} calculated from ultrasonic measurements at different frequencies demonstrate very good consistency with values η_0 (with a deviation of about 10%), notwithstanding the different physical or chemical properties of liquids to be investigate. For example, the results presented in [5] for di-n-butyl phthalate in the frequency range between 23 MHz and 302 MHz show that both viscosity values $\eta_0$and η_{us} are equal ($\eta_0 = 16.6*10^{-3}$ Pa∗s) at ultrasonic frequencies less than 100 MHz with a measurement error of less than 10%. With a further increase in the measurement frequency, the measured value η_{us} decreases ($\eta_{us} = 14.7^{-3}$ Pa∗s at 302 MHz). Therefore we can assume that there are two factors ensuring the fulfillment of the condition $\eta_{us} = \eta_0$ in liquids. These factors include sufficiently low numerical values of η_0 (less 0.015⋯0.02 Pa∗s) and the absence of processes leading to a frequency dependence of the viscosity coefficient in the investigated frequency range. However, these issues have not been adequately studied and require further consideration.

In contrast to the liquids of the first group, the liquids of the second group are characterized by frequency dependence of the viscosity coefficient and demonstrate significant differences between the values of η_0 and η_{us} ($\eta_{us} < \eta_0$). This inequality increases with increasing frequency. The typical viscosity values η_0 of liquids in which the condition $\eta_{us} < \eta_0$ has been observed are $\eta_0 \geq$ (0.1–0.2) Pa * s. In other words, the capillary (rotation) shear viscosity of second group liquids is in essence greater than the viscosity of the first group.

Since only small amplitudes of deformation are realized in all ultrasonic measurements, it can be assumed that the decisive role in the emerging difference is due to the significantly higher frequency range of shear deformations used in ultrasonic measurements in comparison to rotational and capillary methods. Therefore, the shear viscosity calculated from ultrasonic measurements (η_{us}) can be called high-frequency shear viscosity as well.

The discussion shows that the well-known classification of liquids (Newtonian or non-Newtonian liquids) should be more accurately determined in order to use and describe the results of ultrasonic shear viscosity measurements at which the effect of the frequency increase doesn't simply manifest itself as a deviation from the proportional relationship between the viscous tensor and shear strain rate.

2. The classification criterion of liquids based on acoustical shear impedance measurements.

The most reliably established experimental result after numerous ultrasonic measurements in liquids is the proportionality of the viscous tensor σ_{ik} created by an ultrasonic wave to the shear rate$\partial v_i/\partial x_k$ (wherein x_k is the wave propagation direction written in Cartesian coordinates). This proportionality was observed in polymers, their solutions and in numerous other liquids as well. Investigations in a broad frequency range from hundreds of kilohertz to a few megahertz showed no deviation from proportionality, so long as the relative deformations had not exceeded 0.01 [19]. Recently, these results were confirmed by measuring shear impedance in glycerine at 1.0 MHz, 1.7 MHz and 2.5 MHz [20]. It was shown that the measured acoustical liquid impedance remained constant at all investigated frequencies with a measurement error less than 1%, although the excitation voltage at the ultrasonic transducer was changed by a factor of three. Therefore, it can be assumed that such proportionality of the high-frequency mechanical stress to the shear strain rate during ultrasonic measurements is the experimentally confirmed result both for Newtonian and non-Newtonian liquids, if ω does not change.

When the x-axis coincides with the propagation direction of the incident bulk shear wave and the y-axis coincides with the wave displacement direction, the Navier-Stokes equation and the viscous tensor σ_{vis} can be written in the scalar form [1].

$$\rho\frac{\partial v}{\partial t} = \frac{\partial \sigma_{vis}}{\partial x}, \tag{3}$$

$$\sigma_{vis} = \eta_{us}\left(\frac{\partial v}{\partial x}\right). \tag{4}$$

The function

$$v = v_0 \exp\ i(kx - \omega t) \tag{5}$$

is the solution of Eqs. (3) and (4) system if the wave vector k is defined by relation (6) (v_0 is the oscillation velocity amplitude)

$$k = (1+i)\sqrt{\frac{\omega\rho}{2\eta_{us}}}. \tag{6}$$

The solution of Eq. (3) should satisfy the boundary conditions, both the stress tensor continuity and the particle displacement continuity at the boundary of a solid with liquid. It is then easy to find that

$$\frac{1-R^s_{liq}}{1+R^s_{liq}}=\frac{Z^S_{liq}}{Z^S_{sol}}, \tag{7}$$

$$R^S_{liq}\equiv\frac{(v^s_{sol})_{ref}}{(v^s_{sol})_{inc}},\qquad Z^S_{liq}\equiv i\sqrt{i\omega\rho\eta_{us}},\qquad Z^S_{sol}=\rho_{sol}v^s_{sol}. \tag{8}$$

R^S_{liq} is the complex reflection coefficient; $(v^s_{sol})_{ref}$ and $(v^s_{sol})_{inc}$ are the oscillation velocities in the reflected and incident waves, respectively; ρ_{sol} is the density of a solid; and v^S_{sol} is the shear wave velocity in a solid. We note that relationships analogous to (6) and (7) have been considered previously in [6], however with some essential differences.

This relationship (8) plays a fundamental role in the ultrasonic evaluation of liquid shear viscosity for a number of reasons. First, it was obtained without additional assumptions in comparison to the relationships (3) and (4). Moreover Eq. (4) has been, as previously mentioned, experimentally verified. Second, SALI can be easily calculated both from the measured reflection coefficient of the bulk shear wave on the solid-liquid interface and from the absorption coefficient of waveguide waves. Therefore, formula (8) can be used to build the online classification of liquids, if one measures and compares the real and imaginary parts of SALI.

Indeed, if we separate out the real and imaginary parts of formula (8), it is then easy to see that when condition $\mathrm{Re}((Z^s_{liq})_{exp})=\mathrm{Im}((Z^s_{liq})_{exp})$ is fulfilled in a certain frequency range, the ultrasonic viscosity used in the formula (8) must be a real number in this frequency range. This conclusion is confirmed by the known experimental results [2–17] in numerous liquids with low viscosity values, despite their different physical and chemical properties. In addition, the calculated values of the ultrasonic viscosity η_{us} likewise coincide with the values measured using a capillary/rotation viscometer.

In the opposite case, if the measurements show $\mathrm{Re}((Z^s_{liq})_{exp})\neq\mathrm{Im}((Z^s_{liq})_{exp})$, then the viscosity η_{us} used in formula (8) has to be a complex number. Therefore, it can be assumed that the inequality $(\mathrm{Re}(Z^s_{liq})\neq\mathrm{Im}(Z^s_{liq}))$ and the appearance of real and imaginary components of the high-frequency ultrasonic shear viscosity are the characteristic features of liquids related to the second group. It is well known that the above-mentioned properties of the shear viscosity coefficient were introduced in the generalized hydrodynamic model of liquids to interpret the effects observed outside classical hydrodynamics, for example, when considering the necessity of taking into account the presence of relaxation processes [21].

In accordance with generalized hydrodynamics, a viscosity coefficient can be represented as a complex frequency function. Its real part describes dissipative processes and its imaginary part reflects the non-dissipative liquid response. Taking into account that the transport coefficients can be formulated in terms of time correlation functions and assuming that correlation functions relax exponentially as $\exp(-\frac{t}{\tau_d})$) [21], the following equation for the shear viscosity can be obtained:

$$\eta^*(\omega)=\frac{(\eta_0)_M}{1-i\omega\tau_d}=\frac{(\eta_0)_M}{1+\omega\tau_d{}^2}+i\frac{(\eta_0)_M(\omega\tau_d)}{1+\omega\tau_d{}^2}\equiv\eta_1+i\eta_2. \tag{9}$$

Here $(\eta_0)_M$ is the numerical value of the viscosity from the formula (9) at $\omega\tau_d\to 0$, which is likely to coincide with with capillary/rotational viscosity.

The calculation, similar to formula (9), follows from the known Maxwell model [22] as well, although the Maxwell model is not a relaxation model. In the framework of the Maxwell model, if the mechanical stress applied to a liquid depends on time harmonically, then a shear deformation of liquids can be presented as the sum of the viscous component according to Newton's law, and the elastic component according to Hooke's law.

However, the characteristic time τ_M determining the frequency dependency of the shear viscosity in the Maxwell model is described by the function $(\eta_0)_M/G$, where G is the proportionality coefficient between the shear stress and the shear deformation, having the same dimension as the shear modulus in Hooke's law. In what follows, we will use this relation for the numerical estimation of characteristic time τ_M from the experimental data. Substituting formula (9) into (4) and repeating calculations (3)–(8), we obtain as a result for SALI in the Maxwell model

$$(Z^S_{liq})_M=i\sqrt{\frac{i(\eta_0)_M\omega\rho}{2(1-i\omega\tau_M)}}=i\sqrt{\frac{(\eta_0)_M\omega\rho\exp[i(\frac{\pi}{2}+arctg(\omega\tau_M))]}{\sqrt{1+(\omega\tau_M)^2}}} \tag{10}$$

Since the Maxwell model contains only two unknown constants ($(\eta_2)_M$ and τ_M), numerical values of these constants can be calculated from measurement results using the real and imaginary parts of SALI. However, the experimental verification of Eq. (10) as a basis to measure the shear viscosity of liquids is difficult. This is due to insufficient experimental data at the present time in which, as a rule, only the modulus of the shear impedance (or the modulus of the shear conduction) is measured.

The only systematic experimental study of the dependency $\eta_{us}(\eta_0)$ for chlorinated biphenyl liquids is reported in article [5]. These liquids have similar physical/chemical properties and intermolecular interactions, but the viscosities η_0 measured by a capillary viscometer and the ultrasonic viscosities η_{us} are different ($\eta_0>\eta_{us}$). The real a_R and imaginary b_R parts of the SALI at 40 MHz and 25 °C, together with η_0 for these liquids, were measured in [5] and are presented in Table 1. On the basis of these experimental results, and using formula (10), the shear viscosity $(\eta_0)_M$ and the relaxation time τ_M which correspond to Maxwell model for these liquids can be calculated by equating the experimental values a_R and b_R with the theoretical values resulting from the Maxwell model. It was taken into account that the measured reflection coefficient of the shear wave in the article [5] was given in the form $(R^S_{liq})^{exp}=R^S_{liq}\exp[i(\pi-\Theta)]]$ (wherein $\Theta$is the phase difference of the oscillation velocity that occurs when the incident wave is reflected from the boundary in the absence or presence of a test liquid).

Such processing of results shows the following: formula (10) correctly describes the general tendency in the presentation of inequality $(\eta_0)_M<\eta_0$ (it appears when the shear viscosity η_0 increases and its value exceeds several tenths of Pa * s). However, some of the conclusions which follow from formula (10) differ from the observed experimental results not only quantitatively but also qualitatively.

For example, processing the experimental results for Aroclor 1232 and Aroclor 1248 shows that $\eta_0\approx(\eta_0)_M$ for Aroclor 1232, whereas for Aroclor 1248 $\eta_0>(\eta_0)_M$, although the condition $\omega^2\tau^2_M\ll 1$ is satisfied for both liquids (Table 1), and this means that $(\eta_0)_M$ must be independent from frequency. Taking into account that the measured capillary viscosity value η_0 of Aroclor 1248 is approximately 10 times more than that of Aroclor 1232, the received experimental result can be interpreted as an indication that if capillary viscosity η_0 is sufficiently large, then the observed difference between η_0 and the calculated ultrasonic viscosity is due not only to the value $\omega\tau_M$, but also to the influence of some internal process in the liquid. Moreover, in accordance with the experiment for Aroclor 1254 and for Aroclor 1260/1254, the real part of the impedance grows and the imaginary part tends to zero, despite the fact that the condition $\omega^2\tau^2_M\gg 1$ is fulfilled and the Maxwell model predicts the tendency to zero of both parts for this case.

It is known that an improvement in the agreement of the theory with the ultrasonic viscosity measurement results can be achieved if it is

Table 1
Comparison of the calculated and measured values of shear viscosity for the Maxwell model.

Substance Aroclor	$\eta_0(Pa\Delta{*}s)$	$a_R\frac{Pa*s}{m}$	$b_R\frac{Pa*s}{m}$	$\omega\tau_M$	$(\eta_2)_M(Pa{*}s)$
1232	0.0155	5399	4865	0.1	0.016
1248	0.288	21,832	17,428	0.23	0.220
1254	8.75	75,767	21,329	1.64	3.08
1260/1254	114.2	105,779	8909	5.9	17.0

assumed that the relaxation processes manifested in liquids are characterized by a certain distribution function of relaxation times. Such an approach is often used to interpret ultrasonic measurements in polymers and their solutions. The rationale is that their molecules can be represented as a chain consisting of monomer units. A large number of factors can influence the motion of such a chain: the excitation of harmonics, differences in the lengths of chain segments, etc. This causes the appearance of a set of relaxation times. Since the distribution of the relaxation times affects the calculated value of the ultrasonic shear viscosity, an appropriate distribution function can be chosen to achieve the best agreement between the calculations and the experiment.

This approach made it possible to obtain suitable agreement between the theoretical and measured results in silicone oils with a shear viscosity up to 0.2 Pa∗s and in a frequency range of 0.5–0.75 MHz [17]. However, it should be noted that the inequality $\eta_{us} < \eta_0$ was also observed in viscous liquids that are neither polymer solutions nor polymers and in which the presence of a chain structure is unlikely, such as, for example, glycerol [22] and calibration standard liquids N350 and S600 [7].

Unfortunately, as a rule, the ultrasonic viscosity measurements are performed only at one frequency or in a very narrow frequency range. The exceptions are the ultrasonic viscosity measurements in glycerin reported in article [22]. The shear viscosity was calculated from the attenuation coefficient of horizontally polarized plate waves at frequencies 1.0 MHz, 1.67 MHz, and 2.50 MHz (the water content did not exceed ~1%). It was found that the calculated ultrasonic viscosity values did not exceed roughly half of the value of 0.91 Pa * s that was obtained by measurements with the rotational viscometer for this liquid [22]. As for the frequency dependence of η_{us}, the values found differ little from each other at all three frequencies and are within the range (0.52 ∓ 0.05) Pa∗s. It is easy to see that these results cannot be explained in the framework of the Maxwell model (formula (10)). Below, we consider the relaxation model in which the features of the molecular structure characteristic of polymers and their solutions are not used.

3. Cluster relaxation model of high frequency viscosity

The proposed model allows for qualitative interpretations of known experimental results observed in the ultrasonic measurements of shear viscosity in liquids with a sufficiently high viscosity (0.2–0.3 Pa * s). These results include: the inequality $\eta_0 > \eta_{us}$, the frequency dependence $\eta_{us}(\omega)$ manifesting at ultrasonic measurements in the lower megahertz range, and $\eta_{us} \to const$ if $\omega\tau_M \to \infty$. Since high shear viscosity values are accompanied by low values of thermal diffusion, it can be assumed that the thermal motion of structural units in a viscous liquid is slow. This explains the manifestation of relaxation in ultrasonic shear viscosity measurements at low frequencies.

In order to estimate the influence of the relaxation process accompanying the ultrasonic wave in liquids on the shear viscosity measurement, we follow the general methodology proposed by Mandelstam and Leontovich [23]. In accordance with this methodology, it is necessary to introduce some parameter ξ characterizing the liquid state in addition to the thermodynamic parameters. The viscous tensor $\sigma_{vis}(\gamma, \xi)$ becomes a function not only of the shear velocity gradient $\frac{\partial v_y}{\partial x} \equiv \gamma$ but also a function of the parameter ξ (the tensor indexes are omitted).

In order to choose the relaxation parameter ξ for viscous liquids in which relaxation manifestations are observed, it is necessary to note the following: Viscous liquids contain small clusters which are due to the presence of heterogeneous atoms in them, such as carbon, hydrogen, and oxygen [24]. The presence of a set of molecular small clusters of various types is confirmed by the molecular dynamic simulation carried out for liquid glycerin [24]. These clusters are distinguished by their predominant chemical bonds, and, as a result, they have different energies of formation and decay. The formation and decay of clusters are controlled by diffusion processes which, as already noted, are slow and have large characteristic times. Therefore, the following relaxation model can be considered. In the absence of an ultrasonic wave, there is a dynamic equilibrium between the concentrations of different cluster types. The mechanical stresses created by a viscous wave in a near-surface liquid layer with thickness δ break this equilibrium by, for example, changing the heights of the potential barriers separating different molecular clusters.

For simplicity, consider the situation in which there are only two types of clusters that differ in the formation/decay energies. Remaining within the framework of the model, the ratio between the number of molecules combined into the chosen cluster type and the total number of molecules serves as the relaxation parameter ξ (both values are calculated per unit volume).

Since the wave deformation depends on the time as $e^{-i\omega t}$, the instantaneous parameter value ξ also changes over time as $\infty e^{-i\omega t}$, assuming that the ultrasonic wave effect is small. We denote the equilibrium value of the parameter in the presence of an ultrasonic wave for ξ_0. If the liquid is not in equilibrium, then ξ tends to ξ_0. Near the equilibrium state, and when the difference $(\xi - \xi_0)$ is small, the rate of change in ξ can be written as a first-order approximation [1]

$$\frac{\partial \xi}{\partial t} = -\frac{1}{\tau_r}(\xi - \xi_0), \tag{11}$$

wherein τ_r is the relaxation time determined by the height of the barrier which must be overcome to cause cluster decay.

Since the periodic deformation changes both the instantaneous and equilibrium values of the relaxation parameter, we represent each of them as the sum of two components, one of which is equal to the average value of the relaxation parameter and is time independent (the lower index 00), while the other (the upper index ∗) is the periodic time function $e^{-i\omega t}$ [1]

$$\xi_0 = \xi_{00} + \xi_0^*, \tag{12a}$$

$$\xi = \xi_{00} + \xi^*. \tag{12b}$$

Substituting (12a) and (12b) in (11), we have

$$\xi^* = -\frac{1}{\tau_r}(\xi^* - \xi_0^*) = \frac{\xi_0^*}{1 - i\omega\tau_r}. \tag{13}$$

We denote the shear deformation created by the ultrasonic wave $\frac{\partial v}{\partial x} \equiv \gamma$. With respect to Eqs. (12a) and (13), we obtain

$$\frac{\partial \xi}{\partial \gamma} = \frac{\frac{\partial \xi_0}{\partial \gamma}}{1 - i\omega\tau_r}. \tag{14}$$

Taking into account the manifestation of the relaxation process, the viscous tensor becomes a function of both the shear rate γ and the relaxation parameter ξ, and instead of relationship (4), we find

$$\frac{\partial \sigma_{vis}}{\partial \gamma} = \left(\frac{\partial \sigma_{vis}}{\partial \gamma}\right)_\xi + \left(\frac{\partial \sigma_{vis}}{\partial \xi}\right)_\gamma \frac{\partial \xi}{\partial \gamma} \tag{15}$$

Substituting Eq. (14) into (15), the following expression can be written for the ultrasonic viscosity, which is still considered as a coefficient of the proportionality between the viscous tensor and the shear rate $\left(\eta_S^r = \frac{\partial \sigma_{vis}}{\partial \gamma}\right)$

$$\begin{aligned} \eta_S^r(\omega) &= \frac{1}{1 - i\omega\tau_r}\left[\left(\frac{\partial \sigma_{vis}}{\partial \gamma}\right)_\xi + \left(\frac{\partial \sigma_{vis}}{\partial \xi}\right)_\gamma \frac{\partial \xi_0}{\partial \gamma} - i\omega\tau_r\left(\frac{\partial \sigma_{vis}}{\partial \gamma}\right)_\xi\right] \\ &= \frac{1}{1 - i\omega\tau_r}\left[\left(\frac{\partial \sigma_{vis}}{\partial \gamma}\right)_0 - i\omega\tau_r\left(\frac{\partial \sigma_{vis}}{\partial \gamma}\right)_\xi\right] \equiv \frac{1}{1 - i\omega\tau_r}[\eta_0^r - i\omega\tau_r\eta_\infty^r] \\ &= \frac{\eta_0^r + \omega^2\tau_r^2\eta_\infty^r}{1 + \omega^2\tau_r^2} + i\frac{\omega\tau_r(\eta_0^r - \eta_\infty^r)}{1 + \omega^2\tau_r^2} \equiv \eta_1^r + i\eta_2^r. \end{aligned} \tag{16}$$

Here, designations are entered: $\left(\frac{\partial \sigma_{vis}}{\partial \gamma}\right)_0 = \left(\frac{\partial \sigma_{vis}}{\partial \gamma}\right)_\xi + \left(\frac{\partial \sigma_{vis}}{\partial \xi}\right)_\gamma \frac{\partial \xi_0}{\partial \gamma} \equiv \eta_0$ is the shear viscosity in the case of very slow processes when liquid is in an equilibrium state all the time, and $\left(\frac{\partial\sigma_{vis}}{\partial\gamma}\right)_\xi \equiv \eta_\infty$ is the shear viscosity in the case of very quick processes when parameter ξ does not manage to change. It is seen that the ultrasonic viscosity in this relaxation model of the liquid depends on three parameters. To find their numerical values, ultrasonic shear impedance measurements should be carried out on several frequencies.

The relationship in (16) can be generalized to several relaxation processes, such as, for example, if several cluster types are represented. The relaxation in such liquids is characterized by several parallel relaxation processes. Necessary calculations can be performed similarly to the calculations of bulk viscosity carried out in [1]. If we assume that process relaxation times are very different, then each relaxation process can be considered independently of the others, and its contribution is thus determined by the frequency range in which ultrasonic measurements are made.

It is easy to see that the relaxation model allows for the interpretation of many experimental results that contradict the Maxwell model. For example, the relaxation model predicts that $\eta_2^r \to 0$ both when $\omega\tau_r \to \infty$ and $\omega\tau_r \to 0$, while $\eta_1^r \to \eta_0^r = const_1$ when $\omega\tau_r \to 0$, and $\eta_1^r \to \eta_\infty^r = const_3$ when $\omega\tau_r \to \infty$. In other words there are two regions in which the measured ultrasonic viscosity becomes a real frequency-independent number. The first region ("first Newtonian region") is characterized by a higher level of viscosity. The second region ("second Newtonian region") is observed at higher frequencies when $\omega\tau_r \gg 1$, and is characterized by a lower viscosity value.

As for the frequency dependence of ultrasonic viscosity, a simple comparison of the dependence predicted by formula (16) with an experiment is currently impossible. However, some qualitative estimates can be obtained from an analysis of the experimental results presented in [25], in which the structural relaxation in dynamics of glycerol was studied by joint investigations of visible light, UV light and X-ray inelastic scattering. The authors used both their experimental results and literature data for low frequencies (ultrasonic measurements at frequencies of 10 MHz and 27 MHz, calorimetric measurements and an impulsive stimulated thermal scattering study). References to those original works can be found in [25]. Based on these results, an approximating curve was constructed fitting the frequency dependence of the kinematic longitudinal viscosity $(\eta_B + 4\eta_0/3)/\rho$ in the frequency range $10^7 - 10^{12}$ Hz.

It is shown that several characteristic regions can be distinguished on the approximation curve. In the first region, starting at low frequencies and ending at about 100 MHz, the longitudinal viscosity steadily decreases by about a factor of five with increasing frequency. Further, an increase in frequency does not change the longitudinal viscosity up to $10^9 Hz$. At even higher frequencies, the best approximation of the experimental data can be achieved with a Cole-Davidson profile (there are various models [25] to explain the Cole-Davidson profile, but which are not discussed here). Thus, these results obtained can be considered as experimental confirmation of formula (17) in the sense that ultrasound viscosity does not tend to zero and depends weakly on the frequency when $\omega\tau_M \gg 1$.

4. Bulk viscosity estimates using ultrasonic viscosity measurements

On-line measurements of the coefficient of bulk viscosity η_B is of undoubted interest both as a source of information on liquid health in various applications and as an evaluation of physical and chemical kinetic processes in liquids. According to the relationship in Eq. (2), to determinate the bulk viscosity, it is necessary to measure the longitudinal wave absorption coefficient α_l and calculate the Stokes ultrasonic absorption coefficient α_l^{St} caused by shear viscosity in liquids.

By definition, the sound absorption coefficient is the ratio of the time average of energy dissipated per unit time $\bar{E}_{dis}$ to the double value of the average total wave energy in unit time E_Σ [1]:

$$\alpha_l = \left|\frac{\bar{E}_{dis}}{2cE_\Sigma}\right| \tag{17}$$

where

$$\bar{E}_{dis} = \frac{1}{T}\int_0^T \dot{E}_{dis}\,dt \tag{18}$$

$$\bar{E}_\Sigma = \frac{1}{2}\rho u_0^2 V_0 \tag{19}$$

and u_0 is the oscillation wave amplitude in the longitudinal wave, V_0 is the volume of liquid, and T is the period of a longitudinal wave.

The energy loss $\dot{E}_{dis}$ of the wave in a volume V per unit time due to the shear viscosity can be calculated within the generalized hydrodynamic approximation, using the relationships of classical hydrodynamics [1] (without taking into account the contributions of the bulk viscosity and thermal conductivity):

$$(\dot{E}_{dis})^{St} = -\int \sigma_{ik}\frac{\partial v_i}{\partial x_k}dV. \tag{20}$$

Remaining in the same approximation, the expression obtained in classical hydrodynamics for the viscous tensor of a longitudinal wave [1] can be used in the form:

$$\sigma_{ik} = \eta_{us}\left(\frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i} - \frac{2}{3}\delta_{ik}\frac{\partial v_l}{\partial x_l}\right), \tag{21}$$

Supposing that the displacement and propagation directions of the longitudinal wave are directed along the x-axis, we substitute this formula into Eq. (20). Taking into account that the dissipation of the average wave energy per unit time must always be a real positive number, we replace all functions under the integral (20) by their real parts. Since the condition $\alpha_l^{St}\lambda \ll 1$ (λ is the length of longitudinal wave) has to be satisfied (otherwise the Navier-Stokes equation becomes inapplicable [1]), it is easy to see that $\frac{\omega}{c_1} \gg \alpha_l^{St}$. Carrying out the integration in (20), we obtain the following formula for the energy loss of a longitudinal wave caused solely by the shear viscosity.

$$(\bar{E}_{dis})^{St} = -\frac{2\omega^2}{3c_l^2}Re(\eta_{us})u_0^2 V_0 \tag{22}$$

Thus, the Stokes sound absorption coefficient is also calculated from (17), substituting expressions (19) and (22). If $Re(\eta_{us})$ is known, for example, it is calculated in SALI measurements. It is necessary to note that the attenuation coefficient of the longitudinal wave should be measured (if the thermal conductivity can be neglected or its value is known) using the same frequency as the impedance.

5. Conclusion

5.1 As shown by numerous experiments [2–18], all of the investigated liquids can be divided into two groups by comparing the values of η_{us}, which are calculated from the results of ultrasonic measurements with the values measured by capillary (rotation) viscometers. In the first group, the calculated values of η_{us} agree very well with values η_0 (with deviations of about 10%) in the large frequency range, despite the different physical or chemical properties of these liquids. It can be assumed that in order for relationship $\eta_{us} = \eta_0$ to be correct in liquids, two conditions must be satisfied: sufficiently low values of η_0 (less than 0.04 … 0.05 Pa*s) and the absence of processes leading to the frequency dependence of the viscosity coefficient in the frequency range under study. In contrast to the liquids of the first group, the liquids of the second group possess an essentially higher viscosity η_0. They are characterized by the frequency dependence of η_{us} and significant differences between the η_{us} and η_0. Our discussion in part 2 shows that the well-known classification of liquids (Newtonian and non-Newtonian) should be expanded to include the results of high-frequency measurements of shear viscosity.

5.2 To solve the practical problems of measuring liquid parameters and technical diagnostics of a liquid state, an automatic classification of liquids is necessary. The solution is provided by measuring and comparing the real and imaginary parts of the liquid shear impedance. If the real and imaginary parts of the calculated Z_{liq}^{s} are equal $(Re(Z_{liq}^{s}) = Im(Z_{liq}^{s}))$ in a certain frequency range, then the numerical value η_{us} is a real constant number in this frequency range. Otherwise, if the measurements show $Re((Z_{liq}^{s})_{exp}) \neq Im((Z_{liq}^{s})_{exp})$, then the viscosity η_{us} in Eq. (8) must be a complex number. Therefore it can be assumed that the inequality $(Re(Z_{liq}^{s}) \neq Im(Z_{liq}^{s}))$ and appearance of real and imaginary components of the high-frequency shear viscosity are characteristic features of second group liquids.

5.3 A shear viscosity relaxation model is proposed in order to explain the numerous results of ultrasonic viscosity measurements in viscous non-polymeric liquids. Although the model does not assume the existence of molecular structures (chains) inherent in polymers and their solutions, it allows a qualitative interpretation of known experimental results observed in viscous liquids. The model is based on the experimental finding that the composition of viscous liquids includes a large number of different atoms inclined to cluster formation. Typically, these are carbon, hydrogen and oxygen atoms. The molecular dynamic simulation of the structure of liquid glycerin shows that it is characterized by a certain distribution of molecular small clusters, differentiated by types of prevailing chemical bonds. As a result, they have different energies of cluster formation and decay. Since the formation of clusters and their decay are controlled by diffusion processes that are characterized by long characteristic times, their influence should be manifested at low measurement frequencies. In the absence of an ultrasonic wave, there is dynamic equilibrium between concentrations of differing cluster types that is destroyed by the mechanical stresses of the ultrasonic wave.

5.4 Such a relaxation shear viscosity model explains the experimental results that contradict the Maxwell model, in particular the presence of two regions in which the measured ultrasonic viscosity becomes frequency independent. The first region ("first Newtonian region") is characterized by a higher level of viscosity. The second region ("second Newtonian region") is observed at higher frequencies when $\omega\tau_r \gg 1$, and is characterized by a lower viscosity value [26].

5.5 Measurements of ultrasonic viscosity make it possible to determine the Stokes ultrasonic absorption coefficient and, accordingly, the bulk viscosity both of low-viscous and viscous liquids on-line. To find the numerical value of bulk viscosity, it is necessary to measure the real and imaginary components of the shear acoustical impedance of the liquid, to calculate the Stokes sound absorption coefficient, and to measure the absorption coefficient of the longitudinal waves (if the contribution of thermal conductivity can be neglected or is otherwise known).

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultras.2018.10.004.

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