Ultrasonic Behavior of Edible Oils: Correlation With Rheology

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ABSTRACT

Ultrasonic attenuation and velocity are studied for edible oils over the frequency range 2-95 MHz at 19.4 C. Shear and compressional (volume) relaxation spectra are evaluated and compared. Viscoelastic (shear) contribution to attenuation is estimated by Rouse theory. The ratio of volume to shear viscosities decreases with frequency (except for castor oil), indicating that the shear and compressional relaxations are separated on the frequency scale. The results indicate that the molecular rearrangements in the compressional relaxation are long range and require a greater degree of co-operation compared with the shear relaxation. Possible mechanisms for the shear and compressional relaxations are discussed.

INTRODUCTION

Ultrasonic spectroscopy is a non-destructive technique for probing the structure of materials. When applied to liquids, it can give information regarding the dynamics associated with the molecular motion. In the case of polymer melts and solutions, the ultrasonic relaxation process is affected by the molecular conformation, persistence length and normal modes of motion. In the case of small molecules, it is possible to obtain information regarding rotational isomerism and conformational changes. Ultrasonic behavior of synthetic liquids (polymers and small molecules) has been studied extensively (1). While some work has been reported for edible oils, the available data is patchy. Velocities of sound for several oils have been reported by Gouw and Vlugter (2) at 2 MHz. Castor oil has high attenuation and is used as a standard in the calibration of ultrasonic apparatus. As a result, data for castor oil has been reported by several authors (3,4).

Ultrasonic attenuation has been studied over a wide range of frequency for some vegetable oils by Mikhailov et al. (5), where an interesting attempt was made to link the ultrasonic attenuation with high frequency rheology. Unfortunately, this work is clouded by the fact that the zero shear viscosities for castor oil and soy oil reported seem to be an order of magnitude greater than those reported by other well established sources (6,7). The dependence of attenuation and velocity upon frequency and temperature has been reported by Kuo (8). However, no attempt was made to analyze and interpret the ultrasonic data.

In principle the ultrasonic and rheological behavior are related. However, it is necessary to carry out a wide variety of measurements to establish the connection. In this paper, we report the ultrasonic behavior of five vegetable oils with a view to understanding the dynamics of molecular motion.

MATERIALS AND METHODS

The experiments were carried out on castor oil, olive oil, groundnut oil, safflower oil and rapeseed oil. All the oils were refined oils and were used without further purification.

Methods

Fatty acid compositions of the oils were determined by gas chromatography of the derived methyl esters. 100 mg of the oil were converted to methyl esters of the fatty acids by reaction with 1 ml of 0.05M sodium methoxide in methanol for 30 min at 60 C. After cooling, 20 ml of dilute aqueous sulphuric acid (0.01M) was added, and the precipitated esters were extracted with hexane. The hexane extracts were dried, filtered and the solvent removed by rotary evaporation. Then the esters were dissolved in 2,2,4 trimethyl pentane for gas chromatography.

A Carlo Erba MEGA5160 gas chromatograph fitted with a flame ionization detector was used. 0.5-1 μl of methyl ester solution was injected into a column (2m × 3mm i.d.) packed with 3% SP-2310/2% SP-2300 on 100-120 mesh Chromosorb W-Aw (Supelco Inc., Bellefonte, Pennsylvania). The column oven was maintained at 200 C. Methyl esters were identified by comparison with a mixture of known composition, and percentage compositions were calculated from peak areas using a computing integrator (Spectra-Physics model SP4270).

The shear viscosities were measured as function of shear rate on a Contraves rheometer model 115. This instrument is a rotational viscometer, using a concentric cylinder assembly. Further details of the instrument are given elsewhere (9).

Density was measured on a Paar DMA602 density meter. Approximately 1 ml of oil was introduced in a U tube. The measuring principle of the instrument is based upon the change of the natural frequency of a hollow oscillator when filled with different liquids or gases. There exists a simple relationship between the density of the sample and the natural frequency of the filled oscillator. The accuracy of the measurements is estimated to be 1 part in 10^5.

Ultrasonic measurements were carried out by a pulse-echo technique. Figure 1 shows a schematic diagram of the apparatus. A frequency generator produces an electrical signal at a desired frequency, which is modulated by the pulse generator to give an electrical pulse. The signal then passes through a linear amplifier (which is linear up to 1 volt input). After passing through an impedance matching unit, the signal goes to the ultrasonic transducer. The transducer converts the electrical pulse into an ultrasonic pulse of the same frequency. The ultrasonic pulse passes through the sample, and the attenuated pulse is picked up by the receiver which reconverts it into an electrical pulse. The attenuated signal, after passing through an amplifier and an attenuator, is displayed on an oscilloscope in the form of echoes. The attenuator is calibrated in 1 db steps. When

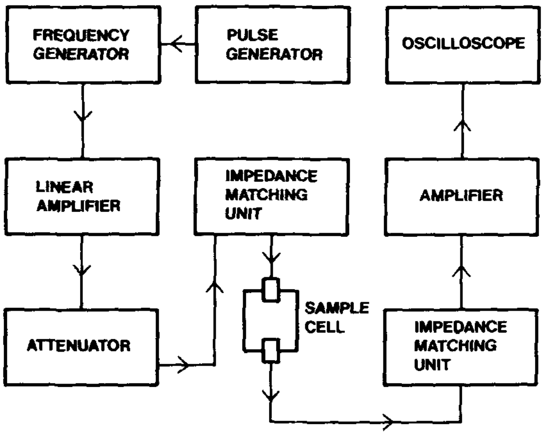

FIG. 1. Schematic diagram of the ultrasonic apparatus.

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attenuation is applied in 1 db steps, the height of the echo can be varied. The height is brought back to the original value by changing the electrode separation. Thus, attenuation can be measured as a function of electrode separation. A straight line is fitted through the two sets of data points by regression analysis, and the attenuation coefficient α is given by the slope of the line. The entire procedure is repeated at several different frequencies to give the dependence of α upon f. The velocity is measured by superimposing the unmodulated input wave upon the output wave and measuring separation between the nulls. A detailed description of the technique is given elsewhere (10).

The ultrasonic transmitter and receiver used in this case were x cut quartz crystals with a fundamental resonant frequency of 5 MHz. The measurements could be made at the fundamental frequency as well as odd harmonics, and the upper limit for the oils was 95 MHz.

A slightly different technique was used for measurements down to 2 MHz. The measuring cell was partitioned into two compartments. One compartment was filled with reference liquid (distilled water in this case), and the other compartment was filled with the oil to be measured. The distance between the electrodes was fixed. However, both the electrodes could be moved as a unit, thereby changing the relative amount of fluids between them. Details of the technique are described by Carstensen (11). Attenuation measurements at 2,6 and 10 MHz were carried out by this technique.

The overall precision in the attenuation measurements was 2% throughout the entire frequency range. The velocity measurements were accurate to within 10 m/sec. The density, viscosity and ultrasonic measurements were carried out at 19.4 ± 0.1 C.

RESULTS

Table I lists the fatty acid composition of the five oils studied. Except for castor oil, the other oils have similar compositions, the major components being oleic acid and linoleic acid. Based upon these compositions, a weight average molecular weight may be calculated, assuming the oils consist of mostly triglycerides. These molecular weights along with density and viscosity data are summarized in Table II. The data is in broad agreement with previously reported results in the literature (6,8). Figure 2 shows the plots of shear stress vs shear rate. All the plots are linear within experimental error, indicating the Newtonian nature of the oils. The zero shear viscosity η_0 is obtained from the slope of the straight lines (viscosity = shear stress/shear rate).

Figure 3 shows the variation of attenuator reading (high attenuator reading indicates low attenuation) with electrode separation at various frequencies for castor oil. Similar plots were obtained for other oils. The attenuation coefficient, α, is given by the slope of these lines. α is plotted as a function of frequency in Figure 4. Similar

TABLE I

Fatty Acid Composition of Oils

Acid	Castor %	Olive %	Groundnut %	Safflower %	Rapeseed %
Lauric				.355	
Myristic				.19	
Palmitic	1.061	11.16	10.742	6.791	5.749
Hexadecenoic		.857			
Stearic	.536	2.349	2.36	2.186	1.751
Oleic	3.911	71.754	54.52	13.158	27.007
Linoleic	4.895	12.639	24.99	76.418	50.184
Linolenic	.347	.448		.111	8.744
Arachidic			1.246	.349	0.55
Ecosenoic			1.209	.334	1.617
Behenic			2.973		.496
Docosenoic					1.204
Lignoceric			1.259		
12-OH-*cis*-9 octadecenoic	88.84				

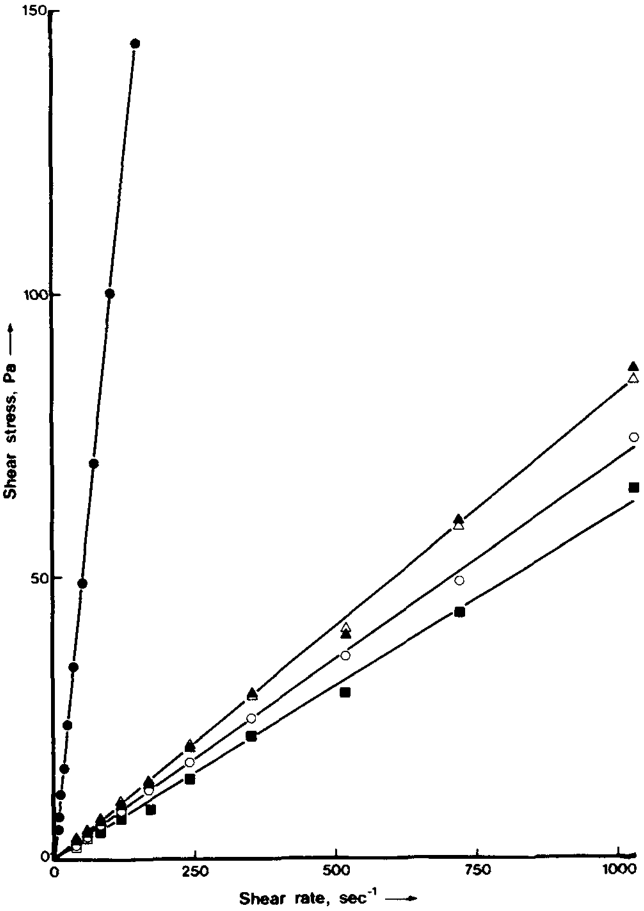

FIG. 2. Plot of shear stress vs shear rate for oils. ●, Castor oil; △, olive oil; ○, groundnut oil; ▲, rapeseed oil, and ■, safflower oil.

TABLE II

Physical and Ultrasonic Properties of Oils at 19.4 C

Oil	Weight average molecular weight	Density kg/m^3	Viscosity Pa.S	Velocity of sound at 5 MHz m/sec	Exponent n ($\alpha = kf^n$) (f in MHz)	Coefficient k
Castor	923	960.25	.902	1494	1.57	11.0
Olive	867	914.20	.082	1469	1.70	1.94
Groundnut	878	914.68	.0743	1483	1.74	1.63
Safflower	876	922.02	.0605	1472	1.76	1.18
Rapeseed	863	920.27	.0859	1478	1.83	1.0

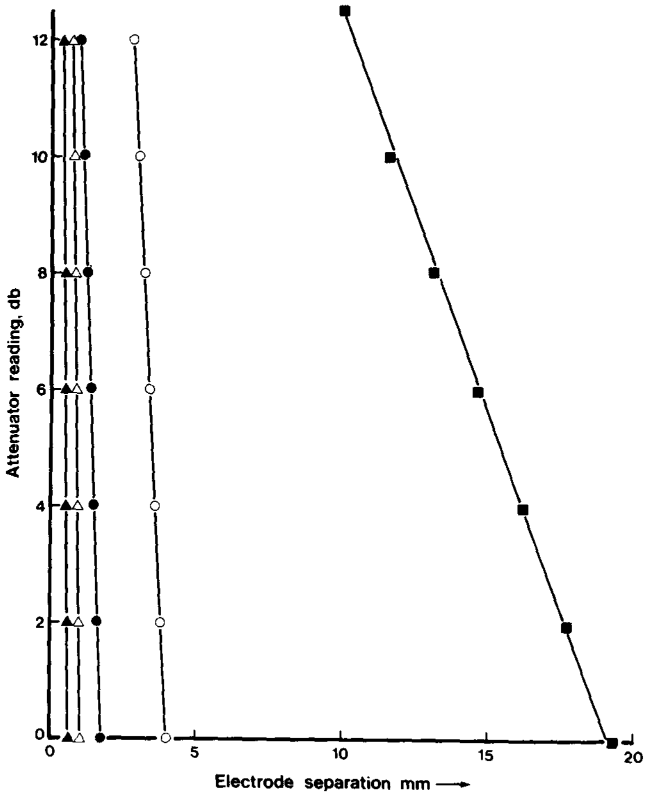

FIG. 3. Attenuator reading as a function of electrode separation for castor oil. ■, 5 MHz; ○, 15 MHz; ●, 25 MHz; △, 35 MHz, and ▲, 45 MHz.

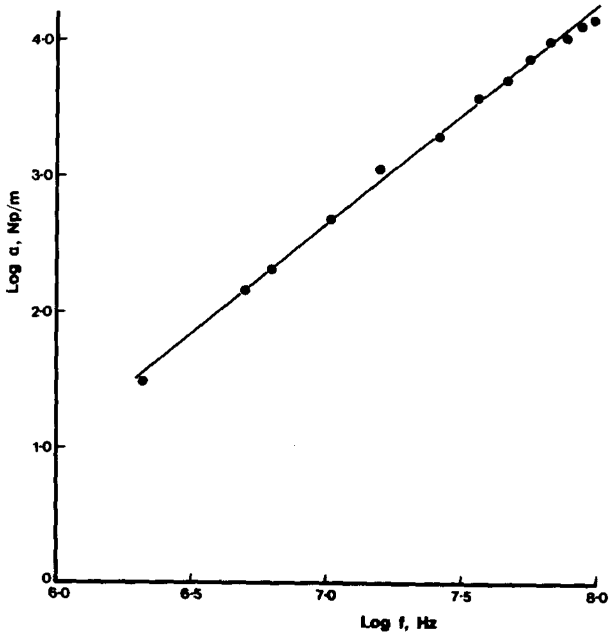

FIG. 4. Variation of attenuation coefficient with frequency for castor oil.

straight lines were obtained for other oils, denoting the power law relationship between α and f. The values of the exponent n and coefficient k (where $\alpha = kf^n$) are listed in Table II, along with the velocity of sound at 5 MHz. For a Newtonian liquid, $\alpha \propto f^2$ if no relaxation takes place. However, $n < 2$ for all the oils studied, indicating that ultrasonic relaxation may be taking place.

DISCUSSION

The shear viscosity is related to the ultrasonic attenuation by the Navier-Stokes equation (12).

$$\alpha/f^2 = \frac{2\pi^2}{\sigma v^3}\left[\eta_v(\omega) + \frac{4}{3}\eta_s(\omega) + \frac{k(\gamma - 1)}{Cp}\right] \qquad [1]$$

where η_v and η_s are the volume viscosity and shear viscosity, respectively, σ is the density, v is the velocity of sound, k is the thermal conductivity, γ is the ratio of the specific heat at constant pressure to that at constant volume and Cp is the specific heat at constant pressure. The last term in the bracket represents the thermal contribution, which is negligible for most liquids. It is necessary to evaluate the shear viscosity $\eta_s(\omega)$ in order to separate out the viscous contribution.

We observed no shear thinning up to the shear rate of 1000 sec^{-1} (Fig. 2). This shear rate is similar to the oscillatory frequency of 1000 Hz. However, the ultrasonic measurements were carried out in the frequency range 2-95 MHz, which is several decades further up the scale. Viscoelastic relaxation may well take place in this region. Ideally, it is necessary to measure the shear viscosity under oscillatory shear in the frequency range 2-95 MHz. Such measurements are possible (e.g. 13,14), but sometimes are subject to large errors. A well established alternative is to estimate the viscoelastic spectrum (15-17). The vegetable oils are low molecular weight liquids, and the viscoelastic behavior may be described by the modified Rouse theory. According to Rouse theory, the dynamic viscosity for a linear small molecule is given by (18):

$$\eta_s(\omega) = \frac{\sigma RT}{M}\,\frac{\tau}{1 + \omega^2\tau^2} \qquad [2]$$

where σ is the density, R is the gas constant, T is the temperature, M is the molecular weight, ω is the frequency and τ is the relaxation time. Oils are multicomponent systems, with several different fatty acid components present as triglycerides. Since the molecular weights of major fatty acid components do not vary significantly, the individual shear stresses may be assumed to be additive in nature and $\eta_s(\omega)$ of the oil may be obtained from summation of the individual components:

$$\eta_s(\omega) = \sigma RT \sum \frac{1}{M_i}\,\frac{\tau_i}{(1 + \omega^2\tau_i^2)}\,w_i \qquad [3]$$

where τ_i and w_i are the relaxation time and weight fraction of the i^{th} species, respectively, and M_i is the molecular weight of the i^{th} species. τ_i may be written in terms of zero shear viscosity and weight average molecular weight $\bar{M}_w$ (18), and it is straightforward to show that for a mixture of linear molecules of different molecular weights,

$$\eta_s(\omega) = \frac{\sigma RT}{\bar{M}_w} \sum \frac{\tau_1\mu_i}{1 + \omega^2\tau_1{}^2\mu_i{}^4} \qquad [4]$$

where μ_i is the dimensionless molecular weight given by $M_i/\bar{M}_w$, M_i being the molecular weight of the i^{th} species, and τ_1 is the relaxation time for $\mu_i = 1$.

This formula holds for linear molecules. Vegetable oils mostly consist of triglyceride molecules which have a 'tuning fork' like structure. A triglyceride may be approximated by a 'star' type molecule with three branches of the star (essentially three fatty acid chains) of about the same length. Several authors have worked out the treatment for branched small molecules (19,20). Essentially, Eqn. [4] may still be applied, but the values of η_o (zero shear viscosity) and τ_1 are not easy to calculate. Ham (21) has worked out the values for $\eta_o/(\eta_o)_{linear}$ and $\tau_1/(\tau_1)_{linear}$ for several topologies. However, the calculations become increasingly inaccurate as the three branches become of comparable length. Hence, τ_1 has to be estimated from experimental data in the present case.

In small molecules, the terminal zone and transitional zone relaxations coincide and are represented by the modified Rouse theory (18). At very high frequencies, molecules cannot change direction in response to the shear field. As a result, there is little molecular motion and a glassy plateau is reached. The viscosity changes very little in this region and cannot be represented by the Rouse theory. As an approximation, the viscosity may be assumed to be constant in the glassy region (22). The total viscosity is then given by

$$\eta_s(\omega) = \frac{\sigma RT}{\bar{M}_W} \sum \frac{\tau_1 \mu_1}{1 + \omega^2 \tau_1{}^2 \mu_i{}^4} \omega_i + \eta_\infty \qquad [5]$$

where η_∞ is the high frequency limiting viscosity. To evaluate the two unknowns (τ_1 and η_∞), it is necessary to know the value of $\eta_s(\omega)$ for two values of ω. The value of $\eta_s(\omega)$ for $\omega = 0$ is the zero shear viscosity and is known. The other value may be obtained by considering the high frequency limit. At sufficiently high frequencies, both the volume viscosity and shear viscosity become very small. However, the dependence of η_v/η_s upon frequency does vary with the nature of the molecule. For soy oil Mikhailov et al. (5) found that η_v becomes negligible compared with η_s at ~90-100 MHz. Ultrasonic attenuation in all the oils studied (except castor oil) is similar to that in soy oil. Other properties of the oils such as major constituents, density, viscosity, molecular weight and velocity of sound are also similar to each other (Table II). Hence, an assumption could be made that the limiting high frequency dependence of η_v/η_s upon ω is also similar. In that case, $\eta_v < \eta_s$ at around 95 MHz for all the oils. η_s can thus be calculated from Eqn. [1] by using the attenuation measurements at 95 MHz and by neglecting η_v at 95 MHz. That value of η_s, along with ω = 95 MHz can be substituted in Eqn. [5] to give the second equation. With two equations and two unknowns, τ_1 and η_∞ can be calculated. These values can then be used to calculate η_s at various frequencies according to Eqn. [4]. Figure 5 shows the calculated variation of viscosity with frequency. Viscous contribution to the total ultrasonic attenuation is then estimated as

$$\left(\frac{\alpha}{f^2}\right)_{\text{viscous}} = \frac{2\pi^2}{\sigma v^3} \bullet \frac{4}{3} \eta_s(\omega) \qquad [6]$$

Figure 6 shows the plots of total attenuation and viscous contribution for olive oil, groundnut oil, safflower oil and rapeseed oil. K is a parameter related to the ratio of volume to shear viscosities and is defined as (15).

$$K = \frac{\frac{4}{3}\eta_s(\omega) + \eta_v(\omega)}{\frac{4}{3}\eta_s(\omega)}$$

$$= \frac{3\sigma v^3 \alpha}{8\pi^2 f^2 \eta_s(\omega)} \qquad [7]$$

K is plotted as function of ω in Figure 7.

While we have not studied the low frequency behavior, K is expected to be constant at low frequencies for small molecules. At low frequencies, the molecule can align as a whole with the changing direction of shear or ultrasonic field. As a result, there is no relaxation and both volume and shear viscosities remain constant. Such a behavior is observed for olive oil, where K decreases very gradually up to 4 MHz, followed by a sharp decrease. For other oils, however, the region of constant K is well below 2 MHz. The viscoelastic behavior of olive oil and rapeseed oil is similar (Fig. 6). However, the ultrasonic behavior differs appreciably, resulting in greatly different values of K. Another noteworthy feature of Figure 6 is the near equivalence of volume and shear viscosities of safflower oil. The behavior of safflower oil is different from the other three oils in that K has a low value and a weak frequency dependence. With the exception of castor oil, the oils have oleic

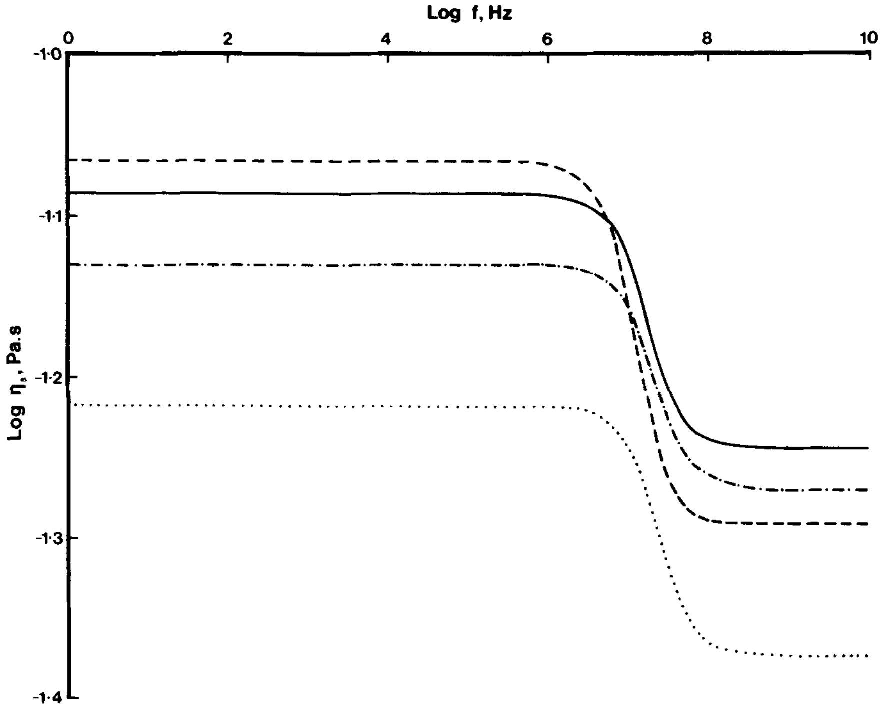

FIG. 5. Shear viscosity as a function of frequency. —— olive oil; – – – – rapeseed oil; —•—• groundnut oil; • • • • • • • safflower oil.

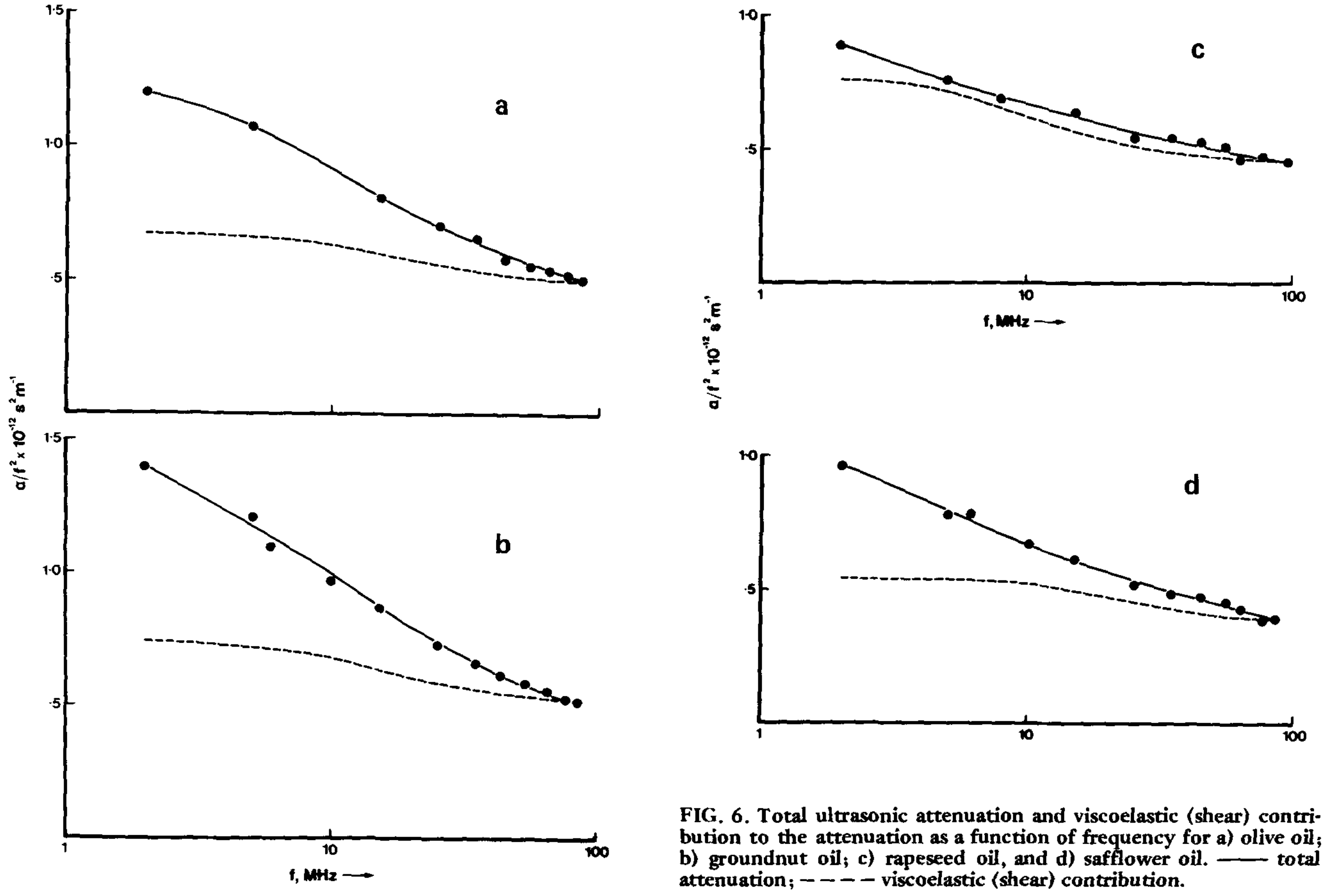

FIG. 6. Total ultrasonic attenuation and viscoelastic (shear) contribution to the attenuation as a function of frequency for a) olive oil; b) groundnut oil; c) rapeseed oil, and d) safflower oil. —— total attenuation; – – – – viscoelastic (shear) contribution.

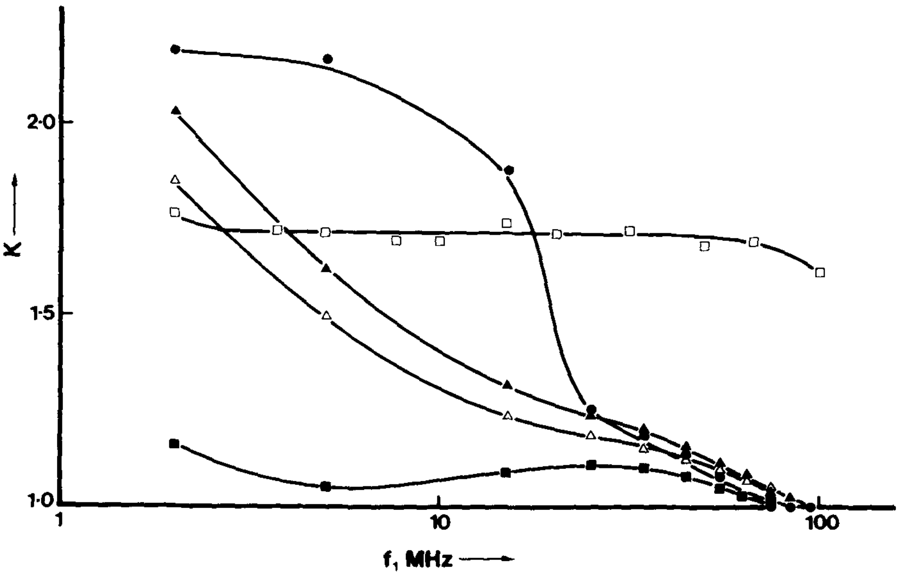

FIG. 7. Plot of K vs frequency for oils (Eqn. [7]). ●, olive oil; ▲, groundnut oil; △, rapeseed oil, and ■, safflower oil; ○, castor oil; K values for castor oil were calculated using the data reported by Mikhailov et al. (5).

acid and linoleic acid as the major constituents. However, safflower oil has the highest linoleic acid content and the lowest oleic acid content of the four oils (Table I). There seems to be a relationship between K and the oleic acid: linoleic acid ratio for the four oils. (The higher the ratio, the higher is the value of K.) More experimental work is needed to determine whether this relationship is confined to the oils studied here or has a more general validity.

For a Newtonian liquid with no ultrasonic relaxation, both η_s and η_v are constant. Hence, K is independent of frequency. Variation of K with frequency implies a separation along the frequency axis of the two relaxation spectra associated with shear and longitudinal wave propagation. Shear relaxation is essentially an isovolumetric process, while longitudinal relaxation is isoentropic, and the activation energies for the two processes may be quite different. For the oils studied, there is a disproportionate reduction of the volume viscosity with increasing frequency (except for castor oil and safflower oil). This would be the case if molecular rearrangements in compressional processes require a greater degree of cooperation than those in shear relaxation. The molecular rotation would then be subject to volume constraints which hinder the achievement of compressional activation energy, while having little effect upon the shear relaxation process. As frequency is increased, this long range cooperation would be less and less forthcoming. This would result in a large decrease in compressional (volume) viscosity accompanied by a relatively small decrease in shear viscosity. Vegetable oils are composed of triglycerides which are rigid, rodlike molecules. If the rods orient in response to the applied shear field, they can slide off each other easily. This molecular reorientation may be responsible for the viscoelastic relaxation. Volume relaxation is slower and more cooperative. This may arise due to intermolecular interactions, where more than one triglyceride molecule moves as a unit in response to the compressional field. Each triglyceride molecule contains three -co- groups, which are slightly polar. There may be weak interactions between the -co- groups from several molecules. Steric interactions also are possible. The fatty acid chains in the triglycerides contain 18-20 carbon atoms. While this is insufficient for entanglements (18), intermolecular penetration may be possible.

In the literature several authors have tried to correlate the velocity of sound with the physical properties of oils (2,23). However, the attempts have been only partially successful, one reason being that the differences in the velocities of individual oils are very small (sometimes less than 0.1%). On the other hand, the ratio of volume to shear viscosities (K) varies considerably among the different oils (Fig. 7). The uncertainty in the present work was in the estimation of shear viscosity. Provided shear viscosity is experimentally measured at high frequencies, it should be possible to correlate K with the physical properties. This could then possibly be used to identify the different oils, the advantage over the velocity technique being that one is dealing with large differences in K.

The above argument does not apply to castor oil, where matters are complicated by the presence of OH groups within the fatty acid chains. Strong intermolecular interactions are expected due to the presence of hydroxyl groups, which is reflected in the large ultrasonic attenuation. Both the volume and shear processes require a much greater degree of cooperation. High frequency shear viscosity for castor oil has been measured by Mikhailov et al. (5). Shear relaxation closely follows the volume relaxation, and the value of K does not change appreciably with frequency (Fig. 7). This is in marked contrast to the ultrasonic behavior of other oils.

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