Absorption and dispersion of ultrasonic waves in organic liquids

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Absorption and dispersion of ultrasonic waves in organic liquids are intimately connected with the complex and frequency dependent bulk viscosity coefficient of the liquid, the real part accounting for absorption while the imaginary part for dispersion Earlier relations for the two components of the bulk viscosity are connected through an equation of a circle It is, however, found from existing experimental data that these relations are not strictly valid and some corrections are to be made to these equations in terms of a parameter the value of which varies between 0 and 1 Values of this parameter are calculated in the case of some liquids at various temperatures Relations connecting the modified expressions for the bulk viscosity are also worked out. Relaxation time associated with the bulk viscosity is evaluated.

1. INTRODUCTION

It is well known that a liquid possesses two viscosities. one is the bulk (or volume) viscosity, designated by η_v and the other is the more familiar shear viscosity, η_s. These properties appear in the equations of hydrodynamics and the bulk viscosity, analogous to the bulk modulus of a solid, is defined as $\eta_d + \frac{2}{3}\eta_s$, where η_d is the coefficient of dilatational viscosity.   The absorption and dispersion of an ultrasonic wave in a liquid is attributed to a large extent to this liquid property, which is represented as complex, *i e.*, $\eta_v{}^* = \eta_1 - i\eta_2$ η_1 is responsible for the absorption of the wave while η_2 accounts for its dispersion and both are frequency-dependent One of the authors (Narasimham 1969) has earlier derived expressions, using step function response of a system to an applied sinusoidal force, for the two components of the bulk viscosity, which are related to each other through a Fourier transformation and can be expressed as

$$\eta_1(\omega) - \eta_1(\infty) = [\eta_1(0) - \eta_1(\infty)] \cdot \frac{1}{1 + \omega^2\tau^2} \qquad \cdot \cdot \quad (1)$$

and
$$\eta_2(\omega) = [\eta_1(0) - \eta_1(\infty)] \cdot \frac{\omega\tau}{1 + \omega^2\tau^2} \qquad \cdots \quad (2)$$

or
$$\eta_v{}^* - \eta_1(\infty) = [\eta_1(0) - \eta_1(\infty)] \cdot \frac{1}{1 + i\omega\tau} \qquad \cdots \quad (3)$$

where ω is the frequency of the wave, $\eta_1(0)$ and $\eta_1(\infty)$ are the values of the in-phase component of the bulk viscosity at $\omega \to 0$ and $\omega \to \infty$, respectively, and τ is the relaxation time associated with one of the dilatational processes. It is the purpose of this paper to see how far these equations can represent experimental values and also to study whether any suitable modifications can be made to the above equations to represent experimental data as correctly as possible

2 Theory

Equations (1) and (2) can also be represented by a single equation as

$$[\eta_1(\omega) - a]^2 + [\eta_2(\omega)]^2 = b^2. \tag{4}$$

where
$$a = \frac{\eta_1(0) + \eta_1(\infty)}{2} \; ; \quad b = \frac{\eta_1(0) - \eta_1(\infty)}{2} \; , \tag{5}$$

i e, the locus of the point (η_1, η_2) is a semicircle, as the frequency of the wave is varied from 0 to ∞ This variation is represented in figure 1, plotting η_1 on the real axis and η_2 on the imaginary axis, in the complex plane.   Here, OA = OB
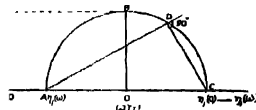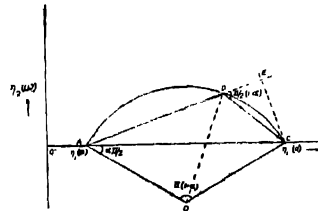
= OC = b = radius of the circle   OO' = a However, this appears to be only an extreme case and in many liquids the observed variation of η_1 and η_2, as ω changes between 0 and ∞, deviates from this semicircular plot (such variation of absorption and dispersion is also observed in dielectrics ; Cole & Cole 1951). The extent of the curve of η_1 against η_2 as ω changes from 0 to ∞ is found to be less than a semicircle, while it still appears to be part of a circle   These curves are drawn for some liquids at varying temperatures (figures 3 to 7 are some representative curves)   In all the cases the whole curve (*i.e.*, $\omega \to$ 0 to ∞) is less than a semicircle. (It cannot be more, since η_1 always decreases with ω while η_2 increases and then decreases with ω and η_1 and η_2 are always positive). Values of η_1 and η_2 are calculated using the following relations (Herzfeld & Litovitz 1959) for ultrasonic absorption and dispersion.

$$\frac{\gamma_{excess}}{\omega^2} = \frac{\eta_1(\omega)}{2\rho V_0{}^3} = \frac{A}{1+\left(\dfrac{\omega}{\omega_c}\right)} \qquad \ldots (6)$$

and $$\omega\eta_2 = 2\rho V_0(V - V_0) \qquad \ldots (7)$$

where V is the wave velocity at any frequency ω, V_0 is that at very low frequencies, γ_{excess} is the excess absorption (i.e , γ_{excess}/ω^2) at low frequencies, ρ is the density of the liquid and ω_c is the frequency at which absorption per wavelength is maxi-
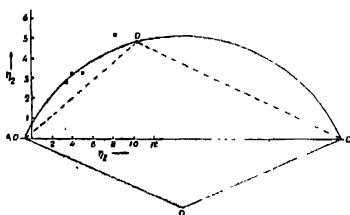

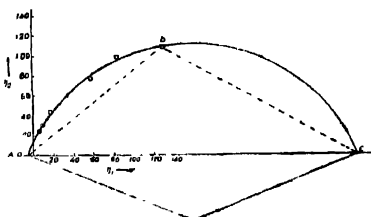FIG.3. η_1 - η_2 CURVE FOR n - PROPYL ALCOHOL AT
TEMPERATURE - 100°C

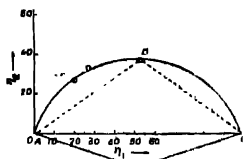FIG. 4. η_1 η_2 CURVE FOR n - PROPYL ALCOHOL AT
TEMPERATURE - 130°C

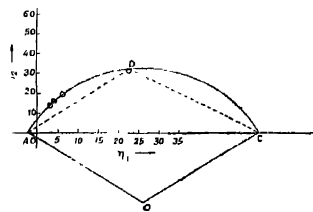FIG5. η_1-η_2 GRAPH FOR GLYCEROL AT 1000 KLS/cm²

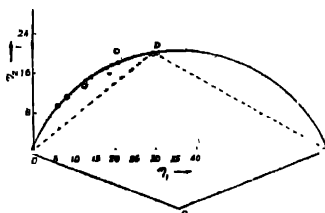FIG-6. η_1 - η_2 CURVE FOR n PROPYL ALCOHOL AT
TEMP 120°C

FIG.7. η_1- η_2 CURVE FOR n -PROPYL ALCOHOL AT
TEMP T = 110°

Figure 2 is a representation of the experimental variation of η_1 against η_2. D is any point on the curve and its coordinates are $\eta_1(\omega)$ and $\eta_2(\omega)$. Since the length of the curve is less than that of a semicircle, $\eta_1(0)-\eta_1(\infty) <$ diameter of the circle, centre O of the circle lies below the $\eta_1(\omega)$—axis, $\angle ADC > \pi/2$, $\angle CDE < \pi/2$ and let $\angle CDE = (\pi/2)(1-\alpha)$, where α can vary between 0 and 1.

Since $OA = OD = OC$, $\angle OAD = \angle ODA$, $\angle ODC = \angle OCD$ and $\angle ADC = \pi/2(1+\alpha) = \angle OAD + \angle OCD$, therefore $\pi/2(1-\alpha) = \pi - \angle ADC = \pi - (\angle ADO + \angle ODC) = \pi - (\angle OAD + \angle OCD) = \pi - (\angle OAC + \angle OCA) - (\angle CAD + \angle ACD) = \angle AOC - \angle CDE$, hence $\angle AOC = \pi(1-\alpha)$ and $\angle OAC = \angle OCA = \alpha\pi/2$. Since $\angle AOC$ is independent of the position of D on the curve and different positions of D correspond to different frequencies, α is independent of ω and is a constant of the liquid at any temperature. For the ideal case (figure 1), $\alpha = 0$.

Since $\angle DEC = \pi/2$, from figure 2, we get

$$AD = \eta_1(\omega)-\eta_1(\infty)-i\eta_2(\omega) = \eta_v{}^*-\eta_1(\infty) \tag{8}$$

$$DC = \eta_1(0)-\eta_1(\omega)+i\eta_2(\omega) = \eta_1(0)-\eta_v{}^* \tag{9}$$

$$\overrightarrow{AD}+\overrightarrow{DC} = \overrightarrow{AC} = \eta_1(0)-\eta_1(\infty) \tag{10}$$

If equations (1) to (4) are true, we get from equations (8) and (10),

$$AD = \frac{\eta_1(0)-\eta_1(\infty)}{1+i\omega\tau} \qquad \frac{AC}{1+i\omega\tau} \tag{11}$$

However, since the experimental curve is not a semicircle, equation (11) is not true.

Now, $DC = DE + i(EC)$, since $\angle DEC = \pi/2$

Therefore $\overrightarrow{AC} = \overrightarrow{AD}+\overrightarrow{DC} = AD+DC\cos\left(\dfrac{\pi(1-\alpha)}{2}\right)$

$$+i\,DC\sin\left(\frac{\pi(1-\alpha)}{2}\right)$$

$$= AD+DC\exp\left[\frac{i\pi(1-\alpha)}{2}\right]$$

$$= AD+DC.i^{1-\alpha} = AD\left[1+\left|\frac{DC}{AD}\right|.i^{1-\alpha}\right] \tag{12}$$

since $\exp(i\pi/2) = i$

Hence $$AD = AC\Big/\left[1+\left|\frac{DC}{AD}\right|.i^{1-\alpha}\right]. \tag{13}$$

For the ideal case (figure 1) $\alpha = 0$ and according to equations (1) to (5) and (8) to (11), $DC/AD = \omega\tau$. However, according to figure 2 $DC/AD \neq \omega\tau$ since equation (4) is not valid, but it is still a function of frequency. The factor $i\omega$ in equation (3) and other equations is a result of the wave equation; the ultrasonic pressure or the velocity and velocity gradient of the particles are proportional to $\exp(i\omega t)$ and in the various operations that precede the derivation of equations (1) to (4), $i\omega$ occurs as a single unit, and α may be considered as a correction to equations (3) or (11) to represent the experimental data correctly. Hence DC/AD may be proportional to $\omega^{1-\alpha}$ and since equations (11) and (13) are same dimensionally, it can be arbitratily fixed that $DC/AD = (\omega\tau)^{1-\alpha}$. Thus equations (3) and (11) have to be corrected as (due to deviation of experiment from (1) and (2))

$$\eta_v{}^* - \eta_1(\infty) = \frac{|\eta_1(0)-\eta_1(\infty)|}{1+(i\omega\tau)^{1-\alpha}} \qquad \ldots \quad (14)$$

Putting $$i^{1-\alpha} = \exp \frac{i\pi(1-\alpha)}{2}$$

$$= \cos \frac{\pi(1-\alpha)}{2} + i \sin \frac{\pi(1-\alpha)}{2}$$

$$\sin \frac{\alpha\pi}{2} + i \cos \frac{\alpha\pi}{2} \qquad \ldots \quad (15)$$

and rationalizing we get

$$\eta_1(\omega) - \eta_1(\infty) = \frac{|\eta_1(0)-\eta_1(\infty)||1+(\omega\tau)^{1-\alpha}\sin \alpha\pi/2]}{1+2(\omega\tau)^{1-\alpha}\sin \alpha\pi/2 + (\omega\tau)^{2(1-\alpha)}} \qquad \ldots \quad (16)$$

and

$$\eta_2(\omega) = \frac{[\eta_1(0)-\eta_1(\infty)](\omega\tau)^{1-\alpha}\cos \alpha\pi/2}{1+2(\omega\tau)^{1-\alpha}\sin \alpha\pi/2+(\omega\tau)^{2(1-\alpha)}} \qquad \ldots \quad (17)$$

Thus the bulk viscosity of a liquid is represented better by equations (16) and (17) rather than by equations (1) and (2). The former reduces to the latter for $\alpha = 0$.

Since $DC/AD = (\omega\tau)^{1-\alpha}$, $1-\alpha$ is the slope of the graph of $\log_{10} DC/AD$ against $\log_{10}\omega$ and intercept on $\log_{10}DC/AD$ axis is $(1-\alpha) \log_{10}\tau$. However α can be determined from the geometry of figure 2 and τ can be calculated using values of DC, AD, ω and α.

According to equations (1) and (2), $\eta_1(\omega)-\eta_1(\infty)$ and $\eta_2(\omega)$ are conjugate to each other and are derived from the same function (Narasimham 1969)

$$\eta_1(\omega) - \eta_1(\infty) = \int_0^\infty G(t) \cos \omega t . dt \qquad \ldots \quad (18)$$

and $\eta_2(\omega)$ $= \int_0^\infty G(t)\,\sin\,\omega t\;dt$ ... (19)

where $G(t)$ $= [\eta_1(0)-\eta_1(\infty)]\;\dfrac{\exp(-t/\tau)}{\tau}$

$$\frac{2}{\pi}\int_0^\infty [\eta_1(\omega)-\eta_1(\infty)]\,\cos\,\omega t\;d\omega$$

$$\frac{2}{\pi}\int_0^\infty \eta_2(\omega)\,\sin\,\omega t\;d\omega \tag{20}$$

The conjugate relationship between $\eta_1(\omega)$ and $\eta_2(\omega)$ which can be derived from the same function, *i.e.*, $G(t)$ in equations (18), (19) and (20) can also be expressed as (Fröhlich 1958),

$$\eta_1(\omega)-\eta_1(\infty) = \frac{2}{\pi}\int_0^\infty \frac{\eta_2(f)f\,df}{f^2-\omega^2} \tag{21}$$

$$\eta_2(\omega) = -\frac{2}{\pi}\int_0^\infty \frac{[\eta_1(f)-\eta_1(\omega)]\omega\,df}{f^2-\omega^2} \tag{22}$$

Or, $\eta_1(0)-\eta_1(\infty) = \dfrac{2}{\pi}\int_0^\infty \eta_2(\omega)d(\log\,\omega)$ (23)

and $\eta_2(0) = 0$

Equations (21) and (22) are independent (Fröhlich 1958) of the form of $\eta_1(\omega)-\eta_1(\infty)$ and $\eta_2(\omega)$, as long as equations (18) and (19) are obeyed. The modified expressions for $\eta_1(\omega)$ and $\eta_2(\omega)$, *i.e.*, equations (16) and (17) are also conjugate relationships and obey the equations of Fourier transformations, *i.e*, it can be shown that

$$\frac{G(t)}{1-\alpha} = \frac{2}{\pi}\int_0^\infty [\eta_1(\omega)-\eta_1(\infty)]\,\cos\,\omega t\;d\omega = \frac{2}{\pi}\int_0^\infty \eta_2(\omega)\,\sin\,\omega t\;d\omega \tag{24}$$

where equations (16) and (17) are substituted for $\eta_1(\omega)$ and $\eta_2(\omega)$. Hence equations (21) and (22) are obeyed by equations (16) and (17) also and it turns out that

$$\frac{2}{\pi}\int_0^\infty \eta_2(\omega)d(\log\,\omega) = \frac{\eta_1(0)-\eta_1(\infty)}{1-\alpha} \tag{25}$$

where equation (17) is substituted for $\eta_2(\omega)$. Equations (24) and (25) may be compared with equations (20) and (23). The integral in equations (23) and (25) can be evaluated by plotting a graph between the experimental values of $\eta_2(\omega)$ and ω while $\eta_2(\omega)$ can be obtained from dispersion data, equation (7). Thus

7   .

the deviation of the experimental values of ultrasonic absorption and disper-
sion from equations (1), (2), (6) and (7) results in a correction of the constant
$\eta_1(0)-\eta_1(\infty)$ It may be noted that : (i) according to equations (1) and (2) the
two components of the bulk viscosity of the medium react to the applied
sinusoidal force with a time lag of a quarter of wave period, while according to
equations (16) and (17) this time has to be multiplied by $(1-\alpha)$, (ii) according to
the former equations the tangent to the curve of η_1 vs η_2 at A or C (figure 1)
is perpendicular to the horizontal axis and the slope is infinite, while according
to the latter equations the tangent is not vertical (figure 2) and the slope is
finite $=\tan \pi/2(1-\alpha)$; (iii) according to both former and latter equations $\eta_2(\omega)$
is maximum at $\omega\tau=1$ and its values are $\frac{1}{2}[\eta_1(0)-\eta_1(\infty)]$ and $\frac{1}{2}[\eta_1(0)-\eta_1(\infty)]$
$\tan \pi(1-\alpha)/4$, respectively.   However, according to equation (1), $\eta_1(\omega)-\eta_1(\infty)$
decreases steadily with ω, while it exhibits maxima or minima according to
equation (16)   It is found that the derivative of $\eta_1(\omega)-\eta_1(\infty)$, equation (16),
is zero when $(\omega\tau)^{1-\alpha}=-\cot \alpha\pi/2$ and $-\tan \alpha\pi/2$ The values of $\eta_1(\omega)-\eta_1(\infty)$
corresponding to these values of $\omega\tau$ are

$$\pm \frac{1}{2}[\eta_1(0)-\eta_1(\infty)]\tan \frac{\alpha\pi}{2} \sin \frac{\alpha\pi}{2}$$
$$1+\cos \alpha\pi/2$$

The negative values of $(\omega\tau)^{1-\alpha}$ can be understood if $(\omega\tau)^{1-\alpha}$ is written as $(\omega\tau)^{1/1-\alpha}$
and the negative value of the square root may be considered; (iv) The dispersion*
of the ultrasonic wave, proportional to $V-V_0$, equation (7), reaches a maximum
value, according to equations (2) and (7), as $\omega\to\infty$ However, according to equa-
tions (7) and (17) this maximum occurs at finite values of ω, depending upon the
constant α.

According to equations (1) and (2) the relaxation time can be expressed as

$$(\omega\tau) = \frac{\eta_2(\omega)}{\eta_1(\omega)-\eta_1(\infty)} \qquad \ldots \quad (26)$$

where $\eta_1(\omega)$ and $\eta_2(\omega)$ are given according to equations (6) and (7).   Since the ab-
sorption which depends upon $\eta_1(\omega)$ decreases with ω, it can be assumed that $\eta_1(\infty)$
$=0$.   Hence,

$$\tau = \frac{V-V_0}{V_0^2 \cdot \gamma_{excess}} \qquad \ldots \quad (27)$$

However, according to equations (16) and (17) and (6) and (7), assuming $\eta_1(\infty)$
$=0$.

$$\frac{V_0^2 \cdot \gamma_{excess}}{(V-V_0)\omega} = (\omega\tau)^{\alpha-1} \sec \frac{\alpha\pi}{2} + \tan \frac{\alpha\pi}{2} \qquad \ldots \quad (28)$$

RESULTS

Values of α are calculated for some liquids at different temperatures, using figures 3 to 7 and similar figures Values of relaxation time τ are also calculated using the relation $(\omega\tau)^{1-\alpha} = DC/AD$ by considering a point of known frequency on figures 3 to 7 and similar curves (figures are not given for all the cases). Values of $\eta_1(0) - \eta_1(\infty)$ are also calculated using equation (25), by plotting a graph between $\eta_2(\omega)$ and log ω and measuring the area under the curve. Figure 8 to 10 are some representative graphs. $\eta_2(\omega)$ is obtained from dispersion data, equation (7). Relaxation times are also evaluated using equations (27) and (28). The various parameters are shown in table 1.

It is found that in some cases η_s is appreciable or even larger than $\eta_1(\omega)$. However, the observed absorption depends upon $\eta_1(\omega) + \frac{4}{3}\eta_s$ and the term $\frac{4}{3}\eta_s$ also is associated with the normal velocity gradient even though η_s is the shear viscosity, according to Navier-Stokes equation (Herzfeld & Litovitz 1959). Hence $\eta_1(\omega) + \frac{4}{3}\eta_s$ is used in place of $\eta_1(\omega)$, where η_s is large It may be seen that there is no appreciable variation of relaxation time with temperature and pressure.
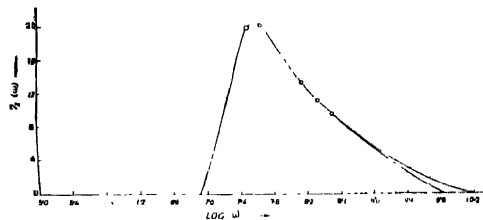

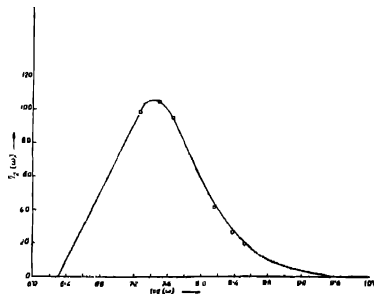FIG. 8 $\eta_2(\omega)$ LOG ω GRAPH FOR n PROPYL ALCOHOL AT TEMP 115°C

FIG.9. $\eta_2(\omega) - $ LOG ω CURVE FOR n PROPYL ALCOHOL AT TEMP -48°C
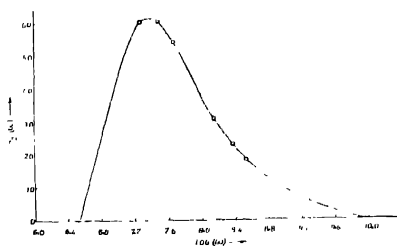
FIG 10 $\eta_1(\omega) - \log \omega$ GRAPH FOR n PROPYL ALCOHOL   AT TEMPERATURE $-125°C$

Table 1.   Ultrasonic parameters for some organic liquids

Liquid	Temperature °C	α	$\tau \times 10^9$ according to $\eta_1(0) - \eta_1(\infty)$ eqns (1) & (2) poises		$\tau \times 10^9$ according to eqn. (27)	eqn. (28)
i-propyl alcohol	−100	2667	5 496	3 642	1.498	5.702
	−115	2389	4 282	13.18	2 113	—
	−120	3555	4.178	19 49	2 228	5.763
	−125	1111	3 922	48 39	3.077	3 843
	−130	2445	8 058	54 83	3 998	1 713
	−135	.1778	2 796	92 66	4.878	10.98
	−140	.1889	7 034	80.56	4.897	11.34
	115	0667	6.653	80 79	—	—
	−150	1500	7 387		—	—
Glycerol	28°C 1000 kgs/cm²	1995	1 092		7389	1.137
	28°C 2000 kgs/cm²	1889	1 495	—	.8928	1.307

Experimental data are from Litovitz & Lyon 1956 and She & Madigosky 1968.

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She W. M. & Madigosky W M 1968 *J. Chem. Phys.* **48**, 2810,