

Research Notes

A Study of the Pressure Variation
of Ultrasonic Absorption in LiquidsEine Untersuchung der Druckabhängigkeit
der Ultraschallabsorption in FlüssigkeitenEtude de l'absorption des ultrasons dans les liquides
en fonction de la pression

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1. Introduction

A liquid possesses two viscosities: the bulk viscosity (η_b^*) and the more familiar shear viscosity (η_s). The bulk [1, 2, 3] viscosity is complex and frequency-dependent and arises out of normal (or, compressional) forces between the molecules, while the shear viscosity is due to tangential forces. These forces affect the propagation of an ultrasonic wave through the liquid. There is a time lag between the application of the pressure wave and the response of the medium. This time lag leads to an absorption of the wave and consequent dispersion. The absorption is related to the structural relaxation time (of the liquid), which may be also called the compressional, or, ultrasonic, relaxation time. The absorption and dispersion of the wave, and the structural relaxation time are closely related to the complex bulk viscosity of the liquid and the frequency of the wave. The real part of the bulk viscosity is responsible for absorption of the wave, while the imaginary part is responsible for velocity dispersion. $\eta_b^* = \eta_1(\omega) - i\eta_2(\omega)$. $\eta_b^* \gg \eta_s$ in a large number of cases, although it may not be valid for the high viscosities encountered at low temperatures.

2. Theory

η_1 and η_2 can be expressed as a set of relaxation equations [1], viz.

$$\eta_1(\omega) - \eta_1(\infty) = [\eta_1(0) - \eta_1(\infty)] / (1 + \omega^2 \tau^2), \quad (1a)$$

$$\eta_2(\omega) = [\eta_1(0) - \eta_1(\infty)] [\omega \tau / (1 + \omega^2 \tau^2)], \quad (1b)$$

where $\eta_1(0)$ and $\eta_1(\infty)$ are the values of $\eta_1 = \eta_1(\omega)$ at very low and very high frequencies, $f (= \omega/2\pi)$, τ is the structural relaxation time. According to eq. (1a), $\eta_1(\omega)$ decreases with frequency, since $\eta_1(0)$ and $\eta_1(\infty)$ are independent of ω . Actually, $\eta_1(0) \gg \eta_1(\infty)$, and $\eta_1(0) - \eta_1(\infty) \approx \eta_1(0)$. This is also evident from eq. (3) below, since $(\alpha/\omega^2) \rightarrow 0$, as $\omega \rightarrow \infty$.

Received 10 March 1987,
accepted 1 December 1990.

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Hence, we have

$$\eta_1(\omega) \approx \eta_1(0) / (1 + \omega^2 \tau^2). \quad (2)$$

However, according to the equations of hydrodynamics [2, 3],

$$\eta_1(\omega) + \frac{4}{3} \eta_s \approx \eta_1(\omega) = 2(\alpha/\omega^2)_\omega \rho_0 (v(\omega))^3, \quad (3)$$

where $v(\omega)$ is the velocity at any frequency $\omega (= 2\pi f)$ and α is the amplitude absorption coefficient: ρ_0 is the density of the undisturbed liquid. Here, we are considering only those cases for which $\eta_1(\omega) \gg \eta_s$, i.e., the observed absorption (α) is much greater than the classical absorption (α_{class}), where

$$(\alpha_{\text{class}}/\omega^2) 2 \rho_0 v^3 = \frac{4}{3} \eta_s.$$

Thus $\alpha - \alpha_{\text{class}} \approx \alpha$ and

$$\eta_1(0) = 2 \rho_0 (v(0))^3 (\alpha/\omega^2)_0, \quad (4)$$

where $(\alpha/\omega^2)_0$ and $v(0)$ are the values at very low frequencies ($\omega \approx 0$). Combining eqs. (2), (3) and (4), we have

$$1 + \omega^2 \tau^2 = \eta_1(0) / \eta_1(\omega) = (\alpha/\omega^2)_0 (v(0))^3 / [(\alpha/\omega^2)_\omega (v(\omega))^3]. \quad (5)$$

It may be noted that $\eta_1(0) > \eta_1(\omega) > \eta_1(\infty)$ as discussed above.

From eq. (5) we have:

$$\omega^2 \tau^2 = \frac{(\alpha/\omega^2)_0 (v(0))^3 - (\alpha/\omega^2)_\omega (v(\omega))^3}{(\alpha/\omega^2)_\omega (v(\omega))^3}, \quad (6)$$

and

$$\tau = \frac{1}{\omega} \left[\frac{(\alpha/\omega^2)_0 (v(0))^3 - (\alpha/\omega^2)_\omega (v(\omega))^3}{(\alpha/\omega^2)_\omega (v(\omega))^3} \right]^{1/2}. \quad (7)$$

The relaxation time (τ) is related to the activation energy, or intermolecular potential barrier, by the relation

$$\tau = \tau_0 \exp(W/kT), \quad (8)$$

where τ_0 is a constant, W is the height of the potential barrier, k is the Boltzmann's constant, and T is the Kelvin temperature. Work W must be done to lift a molecule over the potential barrier. If we apply an excess pressure P to the liquid, and if the compressibility of the liquid is X , then the bulk modulus of the liquid, $K = 1/X$, where $K = -P/(dV/V)$. dV is the decrease in the volume, V is the original volume and P is the applied excess pressure. If V is the average volume occupied by a molecule of the liquid, then dV is the decrease in this volume due to the application of the excess P . $P dV$ is the work done by the external pressure P (to compress the volume V by an amount dV). This is also the magnitude of the decrease in the height of the potential barrier (and in the work to be done on the molecule in lifting it over the potential barrier). Hence, only work $(W + P dV)$ (dV is negative) needs to be done to lift the molecule over the potential barrier under the action of an external pressure P . Therefore eq. (8) has to be modified to:

$$\tau_p = \tau_0 \exp[W + P dV / kT], \quad (9)$$

where τ_p is the compressional relaxation time under an external pressure P . Eq. (9) is in accordance with the known variation (decrease) [4] of relaxation time with increasing external pressure. It is well-known that externally applied temperature and pressure decrease the height of the potential barrier, providing an easier escape for the molecules from the

liquid, due to an associated decrease of the intermolecular binding energy, while shifting the molecules to new equilibrium positions. Hence, the sign of $P dV$ in eq. (9) is negative. The ratio dV/V is the same whether V is the volume occupied by a single molecule or the volume of the whole liquid and

$$K = -P/(dV/V) = -PV/dV, \quad (10a)$$

or

$$dV = -PV/K. \quad (10b)$$

Combining eqs. (9) and (10), we have

$$\tau_p = \tau_0 \exp[(W - P^2 V/K)/k T], \quad (11)$$

where V is the molecular volume.

Combining eqs. (7) to (11), we obtain:

$$\omega^2 \tau_0^2 \exp\left[\frac{2(W - P^2 X V)}{k T}\right] = \left[\frac{(\alpha/\omega^2)_0 [v(0)/v(\omega)]^3 - (\alpha/\omega^2)_\omega}{(\alpha/\omega^2)_\omega}\right]_{P,T} \quad (12)$$

where the suffices indicate that the expression within the brackets has to be evaluated at the particular temperature (T) and excess pressure (P). τ_0 and W are constants, independent of pressure and temperature. W is the barrier height at atmospheric pressure. $P = 0$, if there is no external pressure. The suffices 0 and ω refer to very low and reasonably high frequencies. Eq. (12) gives the pressure and temperature variation of the quantity within the brackets, i.e. the relative change in ultrasonic absorption with frequency. It depends upon the ratio $[v(0)/v(\omega)]$ also. Thus ultrasonic absorption, alone, is not expressed explicitly as a function of pressure.

3. Discussion

The validity of eq. (12) can be tested with available data. An important requirement of the liquid to be chosen for this test is that $\eta_b^* \gg \eta_s$, or, $\eta_1(\omega) + \frac{4}{3}\eta_s \approx \eta_1(\omega)$, according to eq. (3). CS_2 is a well-known non-associated liquid, for which the observed absorption (α_{obs}) is accounted for largely by its bulk viscosity, and the absorption due to shear viscosity (α_s) is very small. Using eq. (3), we can see that $(\eta_b + \frac{4}{3}\eta_s)/\eta_s = (\eta_1(\omega) + \frac{4}{3}\eta_s)/\eta_s$ (since $\eta_1(\omega)$ accounts for absorption) $= \alpha_{obs}/\alpha_{sv}$, where α_{obs} is given by eq. (3) and

$$(\alpha_{sv}/\omega^2)_\omega 2 \varrho_0 (v(\omega))^3 = (4/3)\eta_s.$$

Thus,

$$\eta_b/(4/3)\eta_s = (\alpha_{obs} - \alpha_{sv})/\alpha_{sv}.$$

This ratio is about 1100 for CS_2 at ordinary (room) temperature [5] and pressure. Existing data [6] on CS_2 give values of α/f^2 at various frequencies and pressures at $-29^\circ C$ and up to pressures of nearly 1000 kg/cm². These data are reproduced in Table I for ready reference. The shear viscosity (η_s) increases with increasing pressure [7] and decreasing temperature, and hence the absorption due to shear viscosity changes in a similar way. However, the density and velocity also increase [7] with increasing pressure. Thus, the absorption (α/ω^2) due to the shear viscosity, at room temperature, decreases with pressure increasing up to about 1000 kg/cm², and, increases thereafter, due to a very rapid increase [7] in η_s at high pressures (> 1000 kg/cm²). This occurs even in the case of some non-associated liquids such as CCl_4 , toluene etc. It may also be seen from the cited literature [7], that the

Table I. Existing data for CS_2 : (at $T = -29^\circ C$) [6].

f MHz	Pressure			
	1 kg/cm ²	443 kg/cm ²	720 kg/cm ²	987 kg/cm ²
	α/f^2 $\times 10^{17}$ cm ⁻¹ s ²	α/f^2 $\times 10^{17}$ cm ⁻¹ s ²	α/f^2 $\times 10^{17}$ cm ⁻¹ s ²	α/f^2 $\times 10^{17}$ cm ⁻¹ s ²
15.3	5520	4250	3510	2950
25.2	4900	3720	3080	2700
35.3	3870	3200	2660	2450
45.4	3250	2690	2360	2200
55.5	2550	2270	2000	1900
65.5	2300	1860	1715	1600

observed absorption (α_{obs}/ω^2), and hence the bulk viscosity (η_b), decreases with increasing pressure, in the case of these non-associated liquids. The variation with temperature is not great. η_s for CS_2 is 35.5×10^{-4} p and 80×10^{-4} p at $25^\circ C$ and $-63^\circ C$ respectively [8]. Hence, η_s for CS_2 , at $-29^\circ C$ (the case of present interest) is approximately in the middle of this range of values. One can also see from the literature [8] that the observed absorption in CS_2 , which is mainly due to bulk viscosity ($= \alpha_{obs}/\omega^2$), decreases with decreasing temperatures, but these changes are only about 3 or 4 times more (or, less) than the values at room temperature (and pressure). Thus, the value of $\eta_b/\eta_s (\approx \eta_1(\omega)/\eta_s)$, for CS_2 , at $-29^\circ C$, for the range of pressures and frequencies shown in Table I, may still be quite large (about 300 to 400), since this value at room temperature and pressure is more than 1100. Thus the data in Table I satisfy the requirement of $\eta_b \gg \eta_s$, on which eq. (3) is based, and hence, can be used to test eq. (12). However, a word has to be added about the velocity also, since this equation has $(v(0)/v(\omega))$ as a parameter.

Data on the variation of velocity with frequency, in CS_2 , at $-29^\circ C$, at pressures up to 1000 kg/cm², are not available, but some estimates may be made. At 1 kg/cm², at a temperature of $25^\circ C$, CS_2 exhibits very small dispersion (as the frequency is changed from 1 MHz to 190 MHz, the velocity changes [8] from 1142 m/s to 1227 m/s). At $-63^\circ C$ (at 1 kg/cm²), the dispersion is still less (the velocity changes from 1446 m/s to 1481 m/s, over the frequency range $20 \dots 120$ MHz). Hence the dispersion at $-29^\circ C$ may be expected to be less than at $25^\circ C$, other conditions remaining the same. As the temperature is lowered, the behaviour of the liquid is nearer to that of a solid, which exhibits little (or no) dispersion. Likewise, the behaviour of the liquid, at high pressures, may be nearer to that of a solid. Both at high pressures and low temperatures, the shear viscosity is greater, the bulk viscosity is less, the density is greater, and the behaviour in both cases is nearer to that of a solid. Hence, at the high pressures mentioned in Table I, at a temperature of $-29^\circ C$, the dispersion in CS_2 may be less than the dispersion at $25^\circ C$ and 1 kg/cm² pressure. At $25^\circ C$ and a pressure of 1 kg/cm², in CS_2 , the velocity changes from 1144 m/s to 1184 m/s over the frequency [8] range 10 MHz to 67 MHz. Hence, the value of $(v(0)/v(\omega))$ for CS_2 , at $-29^\circ C$, in the pressure range 1 to 1000 kg/cm², in eq. (12), (where $v(0)$ may be taken as the value at about 1 MHz and $v(\omega)$ may be taken as the value at about 70 MHz), can be assumed to be unity, since dispersion decreases, as the pressure is increased, or as the temperature is decreased (although the actual velocity increases, as the pressure is increased, or as the temperature is decreased). Thus velocity dispersion can be neglected.

Table II. Ultrasonic parameters at various pressures at -29°C .

P kg/cm ²	P^2 $\times 10^{16}$ dyn ² cm ⁻⁴	$(\alpha/f^2)_0 = A + B$ $\times 10^{17}$ cm ⁻¹ s ²	$(\alpha/f^2)_f \times 10^{17}$ at $f = 65.5$ MHz	Z	$\ln Z$
1	96×10^{-6}	6080	2300	1.282	0.249
443	18.9	4550	1860	1.203	0.185
720	49.8	3650	1715	1.062	0.060
978	93.5	3040	1600	0.949	-0.053

Eqs. (1 a) and (1 b) assume a single relaxation time, while a distribution of relaxation times may be more reasonable and probable. At high pressures and low temperatures, however, the assumption of a single relaxation time may give fairly good results, since the distribution becomes smaller and smaller, as the temperature is decreased, or, as the pressure is increased.

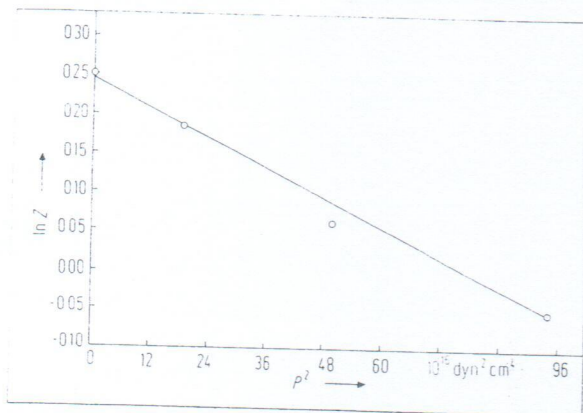
Values of $(\alpha/f^2)_0$ and $(\alpha/f^2)_f$, where $f = \omega/2\pi = 65.5$ MHz, which are needed to test eq. (12), are given in the aforesaid [6] literature and in Table I.

$$(\alpha/f^2)_0 = B + A/[1 + (f/f_0)^2]_{f=0} = B + A,$$

as mentioned in literature [6]. These values are given in Table II. Assuming that $v(0) \approx v(\omega)$, as discussed above, eq. (12) can be written as

$$\ln Z = \ln \left[\frac{(\alpha(\omega^2)_0 - (\alpha(\omega^2)_\omega)^{1/2}}{(\alpha(\omega^2)_\omega)^{1/2}} \right] = \ln(\omega\tau) - P^2 X V/k T. \quad (13)$$

Z is given in Table II, for various pressures, and, τ is the compressional relaxation time at -29°C and at $P = 0$ and is given by eq. (8). (Whether $P = 0$, or atmospheric pressure, will not make any difference, since $W \gg P^2 X V$ for low values of P .) Since the pressure-dependence of the ultrasonic absorption is now considered, the pressure-dependent term is shown separately. A graph of $\ln Z$ vs. P^2 (Fig. 1), gives the value of $\ln(\omega\tau)$ (the intercept) and $X V/k T$ (the slope). From the graph, we can see that $\ln Z$ (for $P = 0$) = $\ln(\omega\tau) = 0.25$, or, $\omega\tau = Z = 1.282$, i.e. $\tau = 1.282/(2\pi \times 65.5 \times 10^6) = 3.159 \times 10^{-9}$ s (at -29°C and atmospheric pressure). This seems to be a reasonable value for the intermolecular structural (or, compressional) relaxation time. The temperature variation of τ (or Z , eqs. (12) and (13)) can give the values of W and τ_0 (eq. (8)). The slope of the graph (Fig. 1) gives the value of

Fig. 1. Variation of $\ln Z$ with P^2 .

$X V/k T$ (eq. (13)), where X is the compressibility of the liquid at -29°C in the pressure range 1 - 1000 kg/cm², V is the molecular volume, k is Boltzmann's constant and $T = 273 - 29 = 244$ K. It may be seen from the graph that the third point is slightly displaced from the straight line. This may be due to the variation in X and V at higher pressures (and hence $X V/k T$ may not remain exactly constant). The slope is $0.245/(93.5 \times 10^{16}) = 2.614 \times 10^{-19}$. Hence, $X V = 2.614 \times 10^{-19} \times 1.38 \times 10^{-16} \times 244 = 8.82 \times 10^{-33}$. The compressibility of CS_2 at room temperature and pressure is about 8.62×10^{-11} cgs units. (It may be still less at high pressures and -29°C .) Hence, the molecular volume $V = 8.82 \times 10^{-33}/8.62 \times 10^{-11} = 1.023 \times 10^{-22}$ cm³ (it should be still more if the reduced value of the compressibility at high pressures and low temperatures is used). At room temperature and pressure a CS_2 molecule has a volume of $76/(1.293 \times 6.03 \times 10^{23}) = 0.9747 \times 10^{-22}$ cm³. Hence the agreement in the values of molecular volumes calculated by ordinary methods and ultrasonic methods seems to be very good. It appears that the effects of high pressures and low temperatures on the shear viscosity at these values of P and T , and velocity dispersion etc., which are possible experimental errors, are not serious, (or all these effects are cancelling each other). In conclusion, it may be seen that ultrasonic methods can be used for the determination of molecular parameters, with fairly good accuracy.

Acknowledgements

The authors wish to thank Prof. Amna Ahmed Ramze, Head of Department of Physics and Dr. Fadhil Al-Saqi, Dean, College of Education for Women, Baghdad University, for their constant encouragement, and to Mrs. S. Bashir for typing the manuscript.

References

- [1] Narasimham, A. V., IEEE Trans. Sonics Ultrason. SU 16 [1969], 182.
- [2] Herzfeld, K. F., Litovitz, T. A., Absorption and dispersion of ultrasonic waves. Academic Press, New York 1959, pp. 34-48.
- [3] Tisza, L., Physical Review 61 [1942], 534, series 2.
- [4] Ref. 2, page 414.
- [5] Ref. 2, page 357.
- [6] Litovitz, T. A., Carnevale, E. A., Kendall, P. A., J. Chem. Phys. 26 [1957], 465.
- [7] Allegra, J., Hawley, S., Holton, G., J. Acoust. Soc. Amer. 47 [1970], 140-146.
- [8] Andrae, J. H., Heasell, E. L., Lamb, J., Phys. Soc. Proc. (London) B 69 [1956], 625.