

Dependence of ultrasonic relaxation on its distribution

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Abstract : There is always a range or distribution in relaxation times rather than a single value. This range in acoustic (or ultrasonic) relaxation times can be understood using the concept of the bulk viscosity coefficient of a liquid, acoustic Cole-Cole plots and a distribution parameter. The ultrasonic relaxation time is found to be a function of ultrasonic velocity, absorption and the distribution parameter. A suitable expression is obtained for the relaxation time which is evaluated at various frequencies for various values of the distribution parameter. These variations are tabulated and discussed.

Keywords : Ultrasonic relaxation, bulk viscosity coefficient, Cole-Cole plot, distribution parameter

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The concept of single relaxation time is only ideal. There is always a range or distribution of relaxation times. There is a distribution of ultrasonic (or acoustic) relaxation times like distribution in dielectric relaxation. The property of complex and frequency dependent bulk viscosity [1] coefficient of a liquid $[\eta_b^*(\omega) = \eta_1(\omega) - i\eta_2(\omega)]$ is very useful in the evaluation of ultrasonic relaxation times and their distribution [2]. The bulk viscosity (less familiar than the usual shear viscosity) is closely associated with normal forces in the liquid, while it is well known that shear viscosity depends upon tangential forces. The bulk viscosity offers resistance to a compression (or expansion) of the liquid, and is closely connected with the propagation of a compressional (or ultrasonic) wave in the liquid. For this reason, the bulk viscosity coefficient is also known as ultrasonic (or volume) viscosity coefficient and is closely connected with the second viscosity [3] coefficient. The real and imaginary parts of the bulk viscosity coefficient account for absorption [4] and dispersion [5] of the compressional waves in the liquid, as detailed [1] below.

The complex bulk viscosity coefficient can be expressed [1] as below.

$$\eta_b^*(\omega) - \eta_1(\infty) = [\eta_1(0) - \eta_1(\infty)] / (1 + i\omega\tau) \quad (1)$$

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

$$\text{and } \eta_2(\omega) = [\eta_1(0) - \eta_1(\infty)] \left[\omega\tau / (1 + \omega^2\tau^2) \right] \quad (1b)$$

$\eta_1(\omega)$ and $\eta_2(\omega)$ are also related with ultrasonic absorption and dispersion by the following Navier-Stokes [4,5] equations of hydrodynamics as follows,

$$\eta_1(\omega) + (4/3)\eta_s = (\gamma/\omega^2) 2\rho_0 V_\omega^3 \quad (2a)$$

$$\omega\eta_2(\omega) = 2\rho_0 V_0 [V_\omega - V_0]. \quad (2b)$$

Eqs. (1) and (2) can be combined to obtain some useful results. $\omega (=2\pi f)$ is the angular frequency of the wave 0 and ∞ refer to very low and very high frequencies of the wave. ρ_0 is the density of the undisturbed liquid. V is the velocity of the wave. γ is the amplitude absorption coefficient of the wave. $i = \sqrt{-1}$ and b indicates bulk. τ is the ultrasonic relaxation time.

However, eqs.(1) assume a single relaxation time [2] and they are only ideal. They do not fit into experimental data. Hence, they need modification [2] as follows :

$$\eta_b^* - \eta_1(\infty) = [\eta_1(0) - \eta_1(\infty)] / [1 + (i\omega\tau)^{1-\alpha}] \quad (3)$$

where α is called the distribution parameter. It can be shown that [2,6] a non-vanishing value of α in eq. (3) leads to a distribution of relaxation times. Eq. (3) reduces to eq. (1) for $\alpha = 0$, which refers to a single [2,6] relaxation time. Using the identity

$$i^{(1-\alpha)} = \sin(\alpha\pi/2) + i \cos(\alpha\pi/2) \quad (4)$$

eq. (3) can be separated into its real and imaginary parts as follows :

$$\eta_1(\omega) - \eta_1(\infty) = \frac{[\eta_1(0) - \eta_1(\infty)] [1 + (\omega\tau)^{1-\alpha} \sin(\alpha\pi/2)]}{1 + 2(\omega\tau)^{1-\alpha} \sin(\alpha\pi/2) + (\omega\tau)^{2(1-\alpha)}} \quad (5a)$$

$$\text{and } \eta_2(\omega) = \frac{[\eta_1(0) - \eta_1(\infty)] [(\omega\tau)^{1-\alpha} \cos(\alpha\pi/2)]}{1 + 2(\omega\tau)^{1-\alpha} \sin(\alpha\pi/2) + (\omega\tau)^{2(1-\alpha)}} \quad (5b)$$

It may be seen that eqs. (5a) and (5b) reduce to eqs. (1a) and (1b) for $\alpha = 0$. If we consider very high frequencies, $\omega^{2(1-\alpha)}\tau^{2(1-\alpha)} > 1$ and 1 can be neglected in the denominators of eqs. (5a) and (5b) without much error. Further, if we consider liquids of low shear viscosity, $(4/3)\eta_s$ can be neglected in comparison with $\eta_1(\omega)$, in eq. (2a). Usually, for many non-associated liquids and for the liquids considered in the present context, $\eta_b \ll \eta_1(\omega)$. We can also see from eq. (2a) that $\eta_1(\omega)$ decreases steadily with frequency. Thus, $\eta_1(\infty) \ll \eta_1(\omega)$. Hence, we can neglect $(4/3)\eta_s$ in eq. (2a) and $\eta_1(\infty)$ in eq. (5a) in the denominators of eqs. (5a) and (5b). Making these approximations we get, since $\eta_1(0) \gg \eta_1(\infty)$, the following expression for $\eta_2(\omega)$,

$$\eta_2(\omega) = [\eta_1(0) \cos(\alpha\pi/2)] / [2 \sin(\alpha\pi/2) + (\omega\tau)^{1-\alpha}] \quad (5c)$$

$$\text{and } \eta_1(0) + (4/3)\eta_s = \eta_1(0) = 2\rho_0 V_0^3 (\gamma/\omega^2). \quad (6)$$

The suffix '0' indicates ' $\omega \approx 0$ '. Substituting eq. (6) for $\eta_1(0)$ in eq. (5c) and using eq. (2b) for $\eta_2(\omega)$, we get after simplification, the following equation for τ .

$$\tau = (1/\omega) \left[V_0^2 (\gamma/\omega^2) (\omega \cos(\alpha\pi/2)) / (V_\omega - V_0) - 2 \sin(\alpha\pi/2) \right]^{1/(1-\alpha)} \quad (7)$$

Eq. (7) gives the average (or weighted average) value of a distribution of relaxation times which may be identified with the experimentally determined value of τ . Eq. (7) gives the experimental value of τ , obtained using experimental values of ultrasonic absorption and velocity. V and (γ/ω^2) can be measured at various frequencies and temperatures.

Experimental values of α can be determined from the acoustic Cole-Cole plots [2,7] similar to dielectric Cole-Cole plots. These are plots of $\eta_1(\omega)$ vs $\eta_2(\omega)$. Their construction, determination of α and τ from their geometry and other details are discussed in earlier literature [2,7]. The values of α vary in most cases, from about 0.1 to 0.5 at various temperatures.

However, in the present case, to study the variation of τ with α , according to eq. (7), arbitrarily chosen values of α (0.1, 0.15, 0.2, 0.25 and 0.3) are used and τ is calculated according to eq. (7) at five different frequencies (f) viz. 1000, 2000, 3000, 5000 and 10000 MHz, at 30° C for 1,2-dibromoethane and pyridine. These values of τ , α and f are given in Table 1.

It may be seen from Table 1 that τ decreases as α increases, according to eq. (7), for 1000 and 2000 MHz, for 1,2-dibromoethane, at 30° C. However, for 3000 MHz, for 1,2-dibromoethane, at 30° C, the variation of τ with α may exhibit a small peak at $\alpha = 0.17$. This exhibition of peak becomes more pronounced for 5000 MHz, and the peak occurs at $\alpha = 0.23$, for 1,2-dibromoethane at 30° C. For pyridine, Table 1 shows that τ decreases with α for 1000 and 3000 MHz. But, for 5000 and 10000 MHz, there is no peak in the variation of τ with α and τ increases with α . Values of τ reported in Table 1, may be considered as the most probable values, or weighted average values, of a distribution. The magnitudes are nearly same for both the liquids. Variation of τ with α can be reasonable and understood. However, variation of τ (with frequency), which is expected to be independent of frequency, is not common and can be understood as follows. At very high frequencies, of the order of 1000s of MHz, variation in γ may not be appreciable for an appreciable change in ω . This leads to an appreciably different value for τ for a small change in frequency (eq. 7).

It may be noted from Table 1, that, $(\omega\tau)^{2(1-\alpha)}$ and 1 are of the same order of magnitude in some cases. But even in these cases, the denominator in eq. (5b), differs only by a factor of about 2, if we neglect and if we do not neglect 1. Thus, there will not be any appreciable change in the values of τ (their order of magnitude), whether we neglect 1, or not, since $(\omega\tau)^{2(1-\alpha)}$ is always greater than 1, for the cases studied here. It may also be noted that it is not necessary to neglect 1, to evaluate τ as a function of α . 1 is neglected in the denominator of eq. (5b) to obtain a relatively simpler expression for $\eta_2(\omega)$ according to

Table 1. Ultrasonic relaxation time (τ) using eq. (7) for arbitrary values of α for 1,2-dibromoethane and pyridine at 30° C at various frequencies.

f (MHz)	α	$\tau \times (10^{-10} \text{ secs})$ at 30° C.	
		for 1,2-dibromoethane	for pyridine
1000	0.10	3.758	3.361
	0.15	3.555	3.127
	0.20	3.253	2.800
	0.25	2.870	2.400
	0.30	2.393	1.926
2000	0.10	1.767	-
	0.15	1.649	-
	0.20	1.490	-
	0.25	1.293	-
	0.30	1.055	-
3000	0.10	1.559	1.860
	0.15	1.576	1.850
	0.20	1.441	1.806
	0.25	1.340	1.727
	0.30	1.184	1.600
5000	0.10	1.419	1.680
	0.15	1.449	1.755
	0.20	1.461	1.807
	0.25	1.453	1.835
	0.30	1.414	1.850
10,000	0.10	-	1.493
	0.15	-	1.630
	0.20	-	1.783
	0.25	-	1.948
	0.30	-	2.120

eq. (7), to show the dependence of τ on α . Hence, eq. (7) is still approximately valid, for the cases studied here, even if $(\omega\tau)^{2(1-\alpha)} \approx 1$.

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