

## Ultrasonic properties of some polyvinyl chloride solutions

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The ultrasonic absorption coefficient ( $\alpha$ ) and velocity ( $v$ ) of solutions of polyvinyl chloride (PVC), in methylethylketone, acetophenone and cyclohexanone have been measured using ultrasonic pulse technique, at a frequency of 800 kHz and at a temperature of 303 K. Shear viscosity coefficient ( $\eta_s$ ) and density ( $\rho$ ) have been measured for these solutions, at this temperature. Relaxation amplitudes  $(\alpha/f^2)_{exp}$  and  $(\alpha/f^2)_{cl}$  and relaxation times,  $\tau_{exp}$  and  $\tau_{cl}$  ( $=\tau_s$ ), Bulk viscosity coefficient ( $\eta_b$ ), adiabatic bulk modulus ( $K$ ), adiabatic compressibility ( $B$ ) and specific acoustic impedance ( $Z$ ) have been calculated from these measurements. The results show that  $\rho$ ,  $\eta_s$ ,  $K$  and  $Z$  increase with concentration of PVC in the three solvents, while  $(\alpha/f^2)_{exp}$  and  $(\alpha/f^2)_{cl}$ ,  $\alpha$  and  $B$  decrease.  $\tau_{exp}$  and  $\tau_{cl}$  show only negligible variation. Their ratio  $(\tau_{exp}/\tau_{cl}) = (\alpha/f^2)_{exp}/(\alpha/f^2)_{cl}$  is almost independent of concentration. Experimental values of  $(\alpha/f^2)$  and  $\tau$  are found to be much larger than classical values, i.e.  $(\alpha/f^2)_{cl}$ ,  $\tau_s$ . The results are discussed in terms of  $\eta_b$  and  $\eta_s$ . It is found that  $\eta_b$  is far greater than  $\eta_s$ .

The variation of ultrasonic velocity ( $V$ ) with frequency ( $f$ ) is termed as dispersion, while reduction in the amplitude of the ultrasonic wave with distance traversed by the wave in the medium is known as absorption. Absorption and dispersion exist together with definite relations between them. There are various causes for absorption and dispersion of the wave. Thermal conductivity of the medium gives a small contribution to absorption, and is usually neglected. Shear viscosity ( $\eta_s$ ) was found to be quite inadequate to explain the observed ultrasonic absorption in the liquid.

Various modern theories, proposed recently, explain the observed absorption adequately. They attribute ultrasonic absorption mainly to intermolecular processes and intramolecular processes. The former is due to various intermolecular (or interatomic) forces, binding energies and relaxations due to structural changes, which lead to absorption and dispersion of the wave. These processes are associated mainly with bulk viscosity ( $\eta_b$ ), bulk modulus ( $K$ ) and compressibility ( $B$ ) of the medium, which become complex and frequency-dependent under the action of a high frequency ultrasonic wave, leading to absorption and dispersion of the wave. Intramolecular processes are not discussed here. This paper discusses experimental results (obtained by the authors) in terms of  $\eta_b$  and  $\eta_s$  of the medium, their variation and

variation of  $B$ ,  $K$  and  $Z$  of three different solutions, with concentration of PVC (solute) in three different solvents.

**Experimental details** — Ultrasonic pulse technique has been used to determine  $\alpha$  and  $v$  in different solutions, obtained by dissolving PVC in methylethylketone, acetophenone and cyclohexanone in various concentrations. The solutions are homogeneous. Density ( $\rho$ ) has been measured for each concentration with a specific gravity bottle-shear viscosity coefficient ( $\eta_s$ ) has been determined for each concentration, with an Ostwald Viscometer, all at the same temperature of 303 K. The frequency ( $f$ ) of the acoustic pulse is 800 kHz. Table 1 gives a sample of the readings and calculations, for determination of the average values of  $\alpha$  and  $v$ , for a concentration of 0.1 (=C%) of PVC in methylethylketone. 'C% = 0.1' indicates a concentration of 1 kg of PVC in 1 m<sup>3</sup> of the solvent.

**Equations used** — The classical (cl) relaxation amplitude, due to shear viscosity ( $sv$ ) is given by:

$$(\alpha/f^2)_{sv} = (\alpha/f^2)_{cl} = (4 \eta_s / 3) (2 \pi^2 / \rho v^3) \quad \dots(1)$$

The classical (shear) relaxation time ( $\tau_s$ ) is given by:

$$\tau_s = (4 \eta_s / 3) / \rho v^2 = (\alpha/f^2)_{cl} (v / 2 \pi^2) = \tau_{cl} \quad \dots(2)$$

Table 1 — Sample readings and calculations to determine the average values of  $\alpha$  and  $v$  in a solution of 0.1% of PVC in methylethylketone

$C\% = 0.1$ ,  $\alpha(\text{average})/m = 57.0$ ,  $v(\text{average}) = 842.0$  m/s. 't' is the time taken by the pulse to traverse a total path 'x'. A is the amplitude of the pulse on the screen (in arbitrary units).  $A_x = A_0$  for  $x = 0$ .  $v \propto 1/t$ .  $\alpha \propto \ln(A_0/A_x)$

$x(\text{m}) \times 10^{-2}$	$t(\mu\text{s})$	Ampl ( $A_x$ )	$v$ (average) m/s	$\alpha/m$
0.00	—	6.5 (= $A_0$ )	—	—
0.50	—	4.90	—	56.5
1.00	11.90	3.70	840.3	56.3
1.50	17.80	2.75	842.0	57.3
2.00	23.70	2.10	843.8	56.4
2.50	29.70	1.50	841.7	58.6

The total (observed) experimental relaxation amplitude, due to both shear and bulk viscosities ( $s$ ,  $bv$ ), is given by:

$$\begin{aligned} (\alpha/\Gamma^2)_{s, bv} &= (\alpha/\Gamma^2)_{ob} = (\alpha/\Gamma^2)_{exp} = \alpha \text{ (experimental)} / (800000)^2 \\ &= (\eta_b + 4 \eta_s / 3) (2\pi^2 / \rho v^3) \quad \dots(3) \end{aligned}$$

The observed compressional relaxation time ( $\tau_{ob}$ ), due to both bulk and shear viscosities, is given by:

$$\tau_{ob} = \tau_{s, bv} = \tau_{exp} = (\alpha/\Gamma^2)_{ob} (v/2\pi)^2 = (\eta_b + 4 \eta_s / 3) / \rho v^2 \quad \dots(4)$$

Shear viscosity also gives a contribution<sup>1-3</sup> to compressional relaxation and absorption of compressional waves in the liquid. From Eqs (1)-(4), we get:  $(\eta_b/\eta_s) = (4/3) \{ [(\alpha/\Gamma^2)_{ob} / (\alpha/\Gamma^2)_{cl}] - 1 \} = (4/3) (\tau_{ob} / \tau_{cl} - 1) \dots(5)$

Eq. (5) can be used to calculate  $\eta_b$  for the solution. It can be compared with  $\eta_s$ .  $\tau_{ob}$  can be compared with  $\tau_s$ .

The adiabatic bulk modulus ( $K$ ), adiabatic compressibility ( $B$ ) and the specific acoustic impedance ( $Z$ ) of the solution are given by:

$$K = 1/B = \rho v^2 \text{ and } Z = \rho v \quad \dots(6)$$

**Results and discussion** — Table 2 gives experimental variation of  $v$ ,  $\alpha$ ,  $\eta_s$  and  $\rho$  with concentration ( $C$ ) of PVC in the three solvents.  $v$  increases with  $C$  in all three solutions. But,  $v$  does not increase linearly with  $C$ . The increase is more at lower concentrations, than at higher concentrations, reaching a maximum (or, saturation) value for infinite concentration (i.e. pure solute). For infinite concentration (i.e. solute-to-solvent ratio  $\rightarrow \infty$ ),

Table 2 — Experimental variation of  $v$ ,  $\alpha$ ,  $\eta_s$ , and  $\rho$  with concentration ( $C$ ) of PVC in three different solvents

Concentration (c) C%	Velocity (v) m/s	Absorption coefficient ( $\alpha$ )/m	Shear viscosity coefficient ( $\eta_s$ ) $\text{Ns/m}^2 \times 10^{-5}$	Density ( $\rho$ ) $\text{kg/m}^3$
PVC in methylethylketone				
0.0	—	—	38.5	806.0
0.1	842.166	57.07	43.1	807.2
0.2	912.000	54.25	48.5	807.8
0.3	974.110	49.50	54.2	808.4
0.4	1028.190	45.61	59.9	809.2
0.5	1100.520	43.08	66.3	809.8
0.6	1154.190	39.02	73.0	810.4
0.7	1221.660	35.79	90.0	811.1
PVC in acetophenone				
0.0	—	—	158.9	1032.7
0.1	1351.351	23.76	175.6	1034.3
0.2	1420.171	22.97	192.5	1035.0
0.3	1474.118	22.04	208.8	1035.6
0.4	1531.210	21.36	225.1	1036.2
0.5	1597.690	20.63	240.4	1036.8
0.6	1645.538	19.84	255.9	1037.5
0.7	1710.609	18.88	274.0	1038.0
PVC in cyclohexanone				
0.0	—	—	179.0	957.0
0.1	1318.117	24.77	198.0	958.2
0.2	1428.571	22.75	222.0	958.8
0.3	1519.875	20.79	245.5	959.4
0.4	1633.504	18.76	269.2	960.1
0.5	1695.889	17.42	293.1	960.7
0.6	1796.510	15.51	317.1	961.3
0.7	1920.106	13.43	342.0	962.3

the velocity is only finite (= velocity in the solute). As the concentration (i.e. solute-to-solvent ratio) increases from 0 to  $\infty$ ,  $v$  increases from solvent-velocity to solute-velocity. Velocity in the solute (a solid) is greater than velocity in the solvent (a liquid). Hence, velocity increases with  $C$ . These variations are alike in all the three cases, while  $(dv/dC)$  differs from one solution to other.

$\alpha$  decreases with  $C$  in all three cases, in a similar fashion. But  $\alpha$  is not proportional to  $(1/C)$ . Because, for infinite concentration,  $(1/C) = 0$ , but,  $\alpha$  has a finite,

Table 3 — Experimental variation of various derived ultrasonic parameters, with concentration (C) of PVC, in three different solvents, using Eqs (1-6) and data obtained by the authors in their laboratory, as given in Table 2

Concentration (C) in C%	$(\alpha/f^2)_{exp}$ (s <sup>2</sup> /m) $\times 10^{-15}$	$(\alpha/f^2)_{cl}$ (s <sup>2</sup> /m) $\times 10^{-15}$	$\frac{(\alpha/f^2)_{exp}}{(\alpha/f^2)_{cl}}$ $\times 10^{+3}$	$\eta_b$ (Ns/m <sup>2</sup> )	$\tau_s$ $\times 10^{-13}$ (s)	$\tau_{exp}$ $\times 10^{-9}$ (s)	$K \times 10^9$ (kg/m s <sup>2</sup> )	$B \times 10^{-10}$ (m <sup>2</sup> /N)	$Z \times 10^5$ (kg/m <sup>2</sup> s)
PVC in methylethylketone									
0.1	89173.00	23.5270	3.7902	2.17753	10.03780	3.8045	0.572501	17.46720	6.7979615
0.2	84765.00	20.8318	4.0690	2.63064	9.62478	3.9163	0.671876	14.88360	7.3670990
0.3	77343.00	19.0905	4.0514	2.92709	9.42097	3.8168	0.767082	13.03640	7.8749052
0.4	71250.00	17.9230	3.9753	3.17414	9.33600	3.7113	0.855469	11.68940	8.3201296
0.5	67325.00	16.1567	4.1670	3.68052	9.00781	3.7536	0.980777	10.19590	8.9119785
0.6	60968.00	15.4192	3.9540	3.84759	9.01593	3.5649	1.079570	9.26294	9.3535233
0.7	55920.00	14.2377	3.9276	4.18837	8.81172	3.4609	1.210500	8.26099	9.9087377
PVC in acetophenone									
0.1	37125.00	18.1068	2.0503	4.79809	12.3959	2.5415	1.88878	5.29440	13.9770230
0.2	35890.00	17.0899	2.1001	5.38769	12.2956	2.5822	2.08745	4.79050	14.6986270
0.3	34437.00	16.5657	2.0788	5.78460	12.3712	2.5717	2.25038	4.44368	15.2659660
0.4	33373.00	15.9256	2.0956	6.28659	12.3538	2.5889	2.42947	4.11610	15.8663980
0.5	32234.00	14.9634	2.1542	6.90172	12.1113	2.6090	2.64654	3.77850	16.5648490
0.6	31000.00	14.5696	2.1277	7.25630	12.1457	2.5842	2.80920	3.55970	17.0716330
0.7	29504.00	13.8793	2.1258	7.76260	12.0279	2.5569	3.03737	3.29230	17.7561210
PVC in cyclohexanone									
0.1	38703.00	23.7523	1.6294	4.29898	15.8609	2.5844	1.66446	6.00795	12.6275600
0.2	35546.00	20.9020	1.7006	5.03082	15.1272	2.5725	1.95673	5.11055	13.6971380
0.3	32484.00	19.1821	1.6935	5.54012	14.7698	2.5013	2.21623	4.51216	14.5816800
0.4	29310.00	16.9305	1.7312	6.21026	14.0107	2.4255	2.56184	3.90344	15.6831080
0.5	27215.00	16.4628	1.6531	6.45641	14.1439	2.3381	2.76301	3.61923	16.2924050
0.6	24234.00	14.9732	1.6185	6.83879	13.6275	2.2056	3.10254	3.22315	17.2698500
0.7	20984.00	13.2132	1.5881	7.23718	12.8829	2.0321	3.54781	2.81863	18.4771800

non-vanishing value, equal to the value of  $\alpha$  in pure solute. For zero concentration,  $(1/C) = \infty$ , but  $\alpha$  is finite, equal to the value of  $\alpha$  in pure solvent.  $\alpha$  is much more in liquids, than in solids, due to various known processes. Hence,  $\alpha$  decreases with  $C$ .  $(d\alpha/dC)$  is negative and differs from solution to solution.

$\eta_s$  increases with  $C$ . The solution is homogeneous and becomes more and more viscous, as the solute is added. The solute makes the solvent more viscous. At low concentrations (studied here),  $\eta_s$  increases uniformly

with  $C$ . But at very high concentrations (not studied here),  $\eta_s$  may increase much faster with  $C$ , since at such high concentrations, the solution may behave like a thick liquid, with much less fluidity, and hence, very high viscosity. The density  $\rho$  increases with  $C$ , for obvious reasons, from the density of the solvent to the density of the solute, as  $C$  increases from 0 to  $\infty$ . Changes in  $\eta_s$  and  $\rho$  are alike in all the three cases.

Table 3 gives the values of various derived parameters, calculated using Eqs (1-6), for the same concentra-

tions ( $C\%$ ), mentioned in Table 2, viz.  $(\alpha/f^2)_{\text{exp}}$ ,  $(\alpha/f^2)_{\text{cl}}$ ,  $[(\alpha/f^2)_{\text{exp}}/(\alpha/f^2)_{\text{cl}}]$ ,  $\eta_b$ ,  $\tau_s$ ,  $\tau_{\text{exp}}$ ,  $K$ ,  $B$  and  $Z$ . Variation of  $(\alpha/f^2)_{\text{exp}}$  is similar to variation of  $\alpha$  (experimental) with  $C$ , as given in Table 2, since  $f$  is a constant, 800 kHz,  $\alpha$ , and hence,  $(\alpha/f^2)_{\text{exp}}$  also, decreases, with  $C$ .  $(\alpha/f^2)_{\text{cl}} = (8\pi^2/3)(\eta_s/\rho v^3)$  also decreases with  $C$ .  $\eta_s$ ,  $\rho$  and  $v$  increase with  $C$ . But,  $\rho v^3$  increases with concentration faster than  $\eta_s$ , leading to a decrease of  $(\alpha/f^2)_{\text{cl}}$  with  $C$ .

The ratio of 'observed' to 'classical' relaxation amplitudes is nearly the same for all concentrations. It is almost independent of  $C$ .  $(\alpha/f^2)_{\text{cl}}$  is obtained by using Eq. (1) and experimental values of  $\eta_s$ ,  $\rho$ , and  $v$ .  $(\alpha/f^2)_{\text{exp}} = (\text{experimental})\alpha/f^2$ , where  $f = 800$  kHz and  $\alpha$  (experimental) is determined as indicated in Table 1.  $\eta_b$  (Table 3) is calculated using Eq. (5). Comparison of  $\eta_b$  (Table 3) with  $\eta_s$  (Table 2) shows that  $\eta_b$  (bulk viscosity values are about 1000 to 5000 times larger than the corresponding  $\eta_s$  (shear viscosity) values.  $(\alpha/f^2)_{\text{exp}} = (\alpha/f^2)_{\text{obs}}$ . This is much larger than  $(\alpha/f^2)_{\text{cl}}$ . Values of  $(\alpha/f^2)_{\text{exp}}$  and  $(\alpha/f^2)_{\text{cl}}$  are shown in Table 3, along with their ratio (1500 to 4000). This ratio is very large ( $\eta_b/\eta_s$ ). Hence  $(\alpha/f^2)_{\text{exp}} \gg (\alpha/f^2)_{\text{cl}}$  and  $\eta_b \gg \eta_s$ . The absorption of the compressional wave in the liquid is largely due to  $\eta_b$ .  $\eta_b$  is related to normal forces in the liquid, while  $\eta_s$  is related to shearing forces in the liquid. Hence,  $\eta_s$  accounts only to a very small extent (and  $\eta_b$  accounts to a very large extent) to absorption of compressional waves in a liquid.  $\eta_b$  is a measure of the resistance offered by the liquid for propagation of compressional waves through the liquid. Ultrasonic waves are compressional waves. As  $\eta_b$  increases, absorption of the ultrasonic wave in the liquid increases. Eqs (1), (3) and (5) explain these results.

The values of  $\tau_s$  and  $\tau_{\text{obs}} (= \tau_{\text{exp}})$  are also given in Table 3. They are connected to  $(\alpha/f^2)_{\text{cl}}$  and  $(\alpha/f^2)_{\text{obs}}$  by Eqs (2) and (4). The relaxation amplitude  $(\alpha/f^2)$  is proportional to the relaxation time ( $=\tau$ ).  $(\tau_{\text{obs}}/\tau_s) \sim (\alpha/f^2)_{\text{obs}}/(\alpha/f^2)_{\text{cl}} \sim$

$(\eta_b/\eta_s)$ .  $\tau_s \ll \tau_{\text{obs}}$ . Relaxation processes lead to absorption of the wave.  $(\alpha/f^2)_{\text{obs}}$  and  $\tau_{\text{obs}}$  are related to structural changes in the liquid, due to propagation of the ultrasonic wave in the liquid. Hence,  $\tau_{\text{obs}}$  may also be called structural relaxation time. Propagation of a compressional wave is associated with compressional relaxation and shear relaxation is negligible. Hence,  $\tau_s \ll \tau_{\text{obs}}$ .

$K (= 1/B)$  increases with concentration. This is understandable. The medium possesses properties closer to those of a solid, as more and more solute is added. Hence, the elasticity of the medium, and hence  $K$  increases, with concentration. Likewise, the acoustic impedance of the medium ( $=Z$ ) also increases with  $C$ , due to the increase in  $\rho$  and  $v$  and also the elasticity of the medium. The medium becomes stiffer with addition of more and more of the solute.

In conclusion, it may be added that the bulk viscosity of liquids and solutions is a very important property of the fluid. This accounts largely for absorption of compressional waves in the medium. Evaluation of bulk viscosity coefficient can lead to an understanding of various interatomic or, intermolecular processes in the medium. Study of its variation with temperature and pressure can lead to structural investigations of the medium.

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