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Editorial

Ultrasonics/Acoustics can play an important role in bridge structures monitoring

Dear Colleagues,

It is my pleasure to greet you on the eve of completion of 40 years of publication of Journal of Pure and Applied Ultrasonics. The journal has been regular since its inception in 1979 and has continuously been gaining popularity among international ultrasonic scientific community. I congratulate all the editorial personnel and publication committee personnel who were associated with the journal over different periods and have made immense contribution in bringing the journal to this status.

I take this opportunity to draw the attention of the readers and through them the other stake holders to the important role the ultrasonic techniques have been playing in bridge structure monitoring, a task which is being felt very urgently in the country for upkeep and maintenance of a large number of its ageing bridges. Many of the old bridges are being used under loads much more than what they were designed for. Moreover they have undergone environment and seismic degradation over years beyond their expected operating life. Recently there have been collapse of bridges accompanied with loss of life and colossal damage to property in Kolkata and Mumbai. Such instances have brought into light the urgent need for continuous monitoring of bridges in the country. Among the measures, ultrasonics /acoustics has a major role to play.

Accelerometers have proven useful in monitoring micro-strain vibrations of structures generated by traffic of environmental conditions. Due to development of damage in bridge the vibration pattern is expected to change. In recent years wireless micro sensing networks with data recording on cloud based systems have been successfully deployed. Fibre Bragg Grating (FBG) sensor offer tremendous potential in monitoring vibrations, various stresses, modification in geometry of bridge structures. The technology of deployment of FBG sensors in bridges is at an advanced stage of development. Acoustic Emission is a technique which has been researched and perfected since two decades and holds great potential.

Impact echo technique involves sounding the bridge structure using hammer and studying the echo pattern which as also velocity and attenuation in Ultrasonic Pulse

Technique undergo changes if any flaws start developing in the structure. These techniques are less expensive but are labour intensive as the testing is localized. Apparently, ultrasonic pulse velocity method has been significantly standardized by ASTM, BSI, etc. and is in use in testing concrete structures, though it is not effective in detecting small cracks and de-lamination of rebar.

Ultrasonic tomography technique is effective in producing images of concrete structures at various depths generating 3-D imaging of inside of concrete structures. It uses an array of point contact transducers. The sounding and image development is carried out based on synthetic aperture. Ultrasonic tomography technique is in use but is useful for examining local structures.

Ultrasonic guided wave (UGW) is another method which involves transmission of guided waves in rebar embedded in concrete structure and offers greater range of testing. Due to delamination or corrosion of rebar from concrete which are the major cause of structure failure, guided waves undergo changes in the transmitted amplitude which are monitored. This technique can be useful for continuous monitoring of reinforced concrete.

Ultrasonic guided wave leakage (UGWL) is the most recent technique which has been successfully investigated. This technique has the highest potential for continuous monitoring of bridges. The leakage of guided waves at the rebar-concrete interface is monitored. The leakage of waves undergoes changes due to delamination, corrosion or crack development at rebar interface. The leakage waves are monitored on the surface using series of receivers.

As enumerated above many of these methods have been introduced in practice world-wide and are further being refined through research. I call upon ultrasonic scientists and stakeholders to take up research and engineering projects to prove the effectiveness of these methods in condition monitoring of bridge structures in our country in order to prevent or mitigate occurrence of mishaps and save lives. I would solicit authoritative articles on the subject for consideration of the Journal of Pure & Applied Ultrasonics.

S.K. Jain — Chief Editor

Ultrasonic attenuation in yttrium monochalcogenides

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The present paper reports ultrasonic properties of yttrium chalcogenides (YCh: Ch=S, Se and Te) along <110> direction in the temperature region 100-500 K. The Coulomb and Born-Mayer potential model is applied to compute the higher order elastic constants. These elastic constants are used to utilise for computing ultrasonic velocity, ultrasonic Grüneisen parameters, thermal conductivity and ultrasonic attenuation. Additionally, the second order elastic constants has been applied to evaluate many mechanical properties such as Young modulus, bulk modulus, Cauchy's relation, Zener's anisotropy factor, toughness to fracture ratio for the prediction about the chosen materials. The YCh follow the Born stability criterion, so these materials are mechanical stable. The toughness to fracture is greater than 0.57, so these materials are brittle in nature. The thermal conductivity is also computed by means of Slack and Berman approach. Finally the temperature ultrasonic attenuation due to phonon-phonon interaction and thermo-elastic relaxation mechanisms has been computed along <110> at room temperature. The achieved results for yttrium monochalcogenides are discussed with similar type of materials.

Keywords: Monochalcogenides, elastic constants, ultrasonic properties, thermal properties.

Introduction

The rare-earth compounds have been attracted for studies on their thermodynamic and lattice dynamical properties due to their unusual behaviour of phonon models in last years¹⁻⁵. The partially filled f-orbital leads to their unusual behaviour. The physical and mechanical properties of rare earth materials can be studied using ultrasonic methods⁶⁻⁷.

There are number of theoretical and experimental studies to analyse the unusual behaviour of yttrium mononictides and monochalcogenides. Vaitheeswaran *et al.*¹ deliberated the structural phase transition of yttrium monochalcogenides under high pressure. Shinde *et al.*² studied structural and phonon properties for yttrium monochalcogenides in rock salt structure using density field theory (DFT). Seddik *et al.*⁵ investigated yttrium chalcogenides for their structural, elastic and high pressure properties using full potential-linear

augmented plane wave (FP-LAPW) plus local orbital method using generalized gradient approximation (GGA). Roedhamer *et al.*⁸ used inelastic neutron scattering for measuring phonon dispersion of yttrium mono-sulphide. Hulliger and Hull⁹ observed super-conductivity in YCh (Ch=S, Se and Te). Tutüncü and Srivastava¹⁰ studied phonon anomalies and superconductivity in rock-salt YS using first principle method by applying plane wave pseudo potential method and DFT. The superconducting behaviour of YS and its phonon spectra were studied by Steiner *et al.*¹¹ which confirmed strong anomalies in the longitudinal- acoustic branch.

The authors did not find any evidence on ultrasonic properties of YCh. There is also no evidence for the thermo-physical study on yttrium monochalcogenides using ultrasonic wave. This motivates us to investigate ultrasonic properties of yttrium monochalcogenides in the temperature range 100-500 K.

The Coulomb and Born-Mayer potential has been applied to evaluate the second and third elastic order constants (SOECs and TOECs) in the temperature region 0-500K for the yttrium monochalcogenides. The SOECs have been utilized to calculate Young's modulus, shear modulus, bulk modulus, Poisson's ratio and Zener anisotropy at room temperature. Further ultrasonic wave velocity and Breazeale's non-linear parameter have been computed along $\langle 110 \rangle$ direction. The thermal conductivity is calculated using Slack and Berman approach¹². Finally, the ultrasonic attenuation due to phonon-phonon interaction and thermo-elastic mechanisms has been analysed using Mason's approach.

Theory

The SOECs and TOECs of YCh were computed using Coulomb and Born-Mayer potentials¹³ at absolute zero. The inter-ionic potential is the sum of Coulomb/electrostatic and Born-Mayer potential/repulsive potential:

$$\phi(r) = \phi(C) + \phi(B) \quad (1)$$

Where $\phi(C)$ is long range Coulomb/electrostatic potential and $\phi(B)$ is the short range Born-Mayer/repulsive potential, given as

$$\phi(C) = \pm(e^2 / r_0) \quad \text{and} \quad \phi(B) = A \exp(-r_0 / b). \quad (2)$$

Here A is the strength parameter, r_0 is the nearest neighbour distance, 'e' is electronic charge, b is the hardness parameter¹⁴.

$$A = -3b \frac{e^2}{r_0} S_3^{(1)} \frac{1}{6 \exp(-\rho_0) + 12\sqrt{2} \exp(-\sqrt{2}r_0)} \quad (3)$$

Leibfried and Hahn¹⁵ developed the lattice dynamical theory. As per this theory the lattice energy alters within temperature. Hence we add vibrational energy contribution to static component of an elastic constant. Then we get SOECs and TOECs at particular temperature

$$C_{IJ} = C_{IJ}^0 + C_{IJ}^{Vib} \quad \text{and} \quad C_{IJK} = C_{IJK}^0 + C_{IJK}^{Vib} \quad (4)$$

The elastic constants at higher temperature are calculated using the method developed by Mori and Hiki¹⁶. The detailed expressions to find out SOECs and TOECs have been given in our recent paper¹⁷.

The shear modulus (G), bulk modulus (B), Zener's anisotropy (A), Poisson's ratio (ν) and tetragonal moduli (C_S) for YCh are also evaluated using SOECs. The expressions for these mechanical constants are given in literature¹⁸.

The Breazeale's non linearity parameter for the distortion to ultrasonic wave propagation is the means of simple harmonic generation of longitudinal wave. Numerically it is negative ratio of non-linearity and linear term in nonlinear wave.

$$\beta = -\frac{3K_2 + K_3}{K_2} \quad (5)$$

K_2 and K_3 are linear combinations of SOECs and TOECs respectively¹⁹.

V_D is the Debye average velocity and is dependent on the longitudinal (V_L) and the shear (V_S) wave velocities with Eq. (6)²⁰:

$$V_D = \left[\frac{1}{3} \left(\frac{1}{V_L^3} + \frac{1}{V_{S1}^3} + \frac{1}{V_{S2}^3} \right) \right]^{-1/3} \quad (6)$$

V_L and V_S are computed with SOECs along $\langle 110 \rangle$ direction using Eq. (7)²¹.

$$\left. \begin{aligned} V_L &= \sqrt{\frac{C_{11} + C_{12} + 2C_{44}}{\rho}} \\ V_{S1} &= \sqrt{\frac{C_{44}}{\rho}} \quad \text{polarized along } \langle 001 \rangle \\ V_{S2} &= \sqrt{\frac{C_{11} - C_{12}}{\rho}} \quad \text{polarized along } \langle \bar{1}\bar{1}0 \rangle \end{aligned} \right\} \quad (7)$$

The thermal conductivity in the materials where there are no charge carriers is due to vibration of lattice ions. In the present work, Mourelli-Slack¹² approach is used to calculate thermal conductivity at a temperature near the Debye temperature of solids. The expression for thermal conductivity is given below:

$$\kappa = \frac{AM_a \theta_D \delta^3}{\gamma^2 T} \quad (8)$$

Where A is a constant having value 3.04×10^{-8} , M_a is the atomic mass (in amu), δ^3 is the volume per atom, γ represents the Grüneisen parameter.

There are several causes of ultrasonic attenuation *i.e.*, electron-phonon (e-p) interaction, phonon-phonon (p-p) interaction and thermo-elastic relaxation mechanisms. But at higher temperature e-p interaction is absent, because of no coupling between the electron and phonon. So p-p interaction and thermo-elastic loss play important role in high temperature regime.

The attenuation of ultrasonic waves may be due to thermo-elastic relaxation mechanism for longitudinal

waves can be evaluated by Mason expression^{22, 23}.

$$\left(\frac{\alpha}{f^2}\right)_{th} = \frac{4\pi^2 \langle \gamma_i^j \rangle^2 \kappa T}{2\rho V_L^3} \quad (9)$$

The Akhieser loss^{24, 25} (loss due to p-p interaction) is expressed as:

$$\left(\frac{\alpha}{f^2}\right)_{Akh.Long} = \frac{4\pi^2 \tau_{th} E_0 (D_L/3)}{2\rho V_L^3} \quad (10)$$

$$\left(\frac{\alpha}{f^2}\right)_{Akh.Long} = \frac{4\pi^2 \tau_{th} E_0 (D_L/3)}{2\rho V_L^3} \quad (11)$$

Where E_0 is the energy density and is a function of $\frac{\theta_D}{T}$.

τ^{th} is the thermal relaxation time and is given as:

$$\tau_{th} = \tau_s = \frac{\tau_{IL}}{2} = \frac{3\kappa}{C_V V_D^2} \quad (12)$$

D is the non-linearity parameter and is obtained using Eq. (13).

$$D = 9 \langle (\gamma_i^j)^2 \rangle - 3 \langle \gamma_i^j \rangle^2 \frac{C_V T}{E_0} \quad (13)$$

Where C_V is the specific heat capacity and is also function of $\frac{\theta_D}{T}$.

Results and Discussion

The SOECs and TOECs are calculated using Eqs. (1-4) using two basic parameters *i.e.* lattice parameter and hardness parameter. The lattice parameter^{1,2,5,6} for YS, YSe and YTe are 5.499Å, 5.736 Å and 6.13Å respectively. The hardness parameter¹⁴ is taken as 0.303 Å for all YCh. The calculated values of SOECs and TOECs for YCh (Ch: S, Se, Te) in the temperature range 0-500K are presented in Table 1.

It is seen that the magnitudes of C_{11} , C_{44} , C_{111} , C_{144} and C_{166} increase 19%, 2.4%, 6%, 3% and 2.3% respectively as we go from 0 K to 500 K. Whereas the magnitude of C_{12} , C_{112} and C_{123} decrease 25%, 23% and 69% respectively at temperature from 0 K to 500 K. The value of C_{456} remains constant. These variations are shown in Table 1. These values are pragmatic with monochalcogenides of lanthanum²³, neptunium²⁴ and europium²⁵. The greater value of elastic constants of YS among the yttrium monochalcogenides under study shows that it is stiffer and stable than the other compounds.

Cousin²⁶ and Hiki & Granato²⁷ proposed that Cauchy relation for SOECs and TOECs at 0K are:

$$C_{12}^0 = C_{44}^0; \quad C_{112}^0 = C_{166}^0; \quad C_{123}^0 = C_{144}^0 = C_{456}^0 \quad (14)$$

Table 1 – Temperature dependent SOECs and TOECs of yttrium monochalogenides (in 10^{10}Nm^{-2}).

Material	Temp.(K)	C_{11}	C_{12}	C_{44}	C_{111}	C_{112}	C_{123}	C_{144}	C_{166}	C_{456}
YS	0	5.27	1.65	1.65	-86.45	-6.74	2.73	2.73	-6.74	2.73
	100	5.54	1.57	1.66	-88.20	-6.44	2.26	2.75	-6.79	2.73
	200	5.70	1.49	1.67	-88.83	-6.14	1.79	2.77	-6.81	2.73
	300	5.88	1.40	1.68	-89.68	-5.83	1.32	2.79	-6.84	2.73
	400	6.07	1.32	1.68	-90.60	-5.52	0.84	2.81	-6.87	2.73
	500	6.26	1.24	1.69	-91.54	-5.22	0.37	2.83	-6.90	2.73
YSe	0	4.86	1.37	1.37	-81.70	-5.58	2.31	2.31	-5.58	2.31
	100	5.09	1.29	1.38	-83.10	-5.27	1.83	2.33	-5.61	2.31
	200	5.26	1.21	1.38	-83.88	-4.97	1.35	2.34	-5.64	2.31
	300	5.44	1.13	1.39	-84.79	-4.65	0.87	2.36	-5.66	2.31
	400	5.62	1.05	1.39	-85.74	-4.34	0.38	2.38	-5.69	2.31
	500	5.81	0.97	1.40	-86.70	-4.03	-0.09	2.40	-5.71	2.31
YTe	0	4.25	1.02	1.02	-74.17	-4.13	1.77	1.77	-4.13	1.77
	100	4.45	0.95	1.03	-75.44	-3.82	1.28	1.78	-4.16	1.77
	200	4.61	0.87	1.03	-76.27	-3.51	0.78	1.80	-4.17	1.77
	300	4.78	0.80	1.04	-77.19	-3.19	0.29	1.81	-4.19	1.77
	400	4.96	0.72	1.04	-78.14	-2.88	-0.19	1.82	-4.21	1.77
	500	5.13	0.64	1.05	-79.10	-2.56	-0.69	1.84	-4.23	1.77

The Cauchy's relations are hold good at 0K as shown in Table 1. The deviation of SOECs and TOECs is found at higher temperatures, which provides information us that the forces become more ionic with increase in the temperature. This type of behaviour was existed in other rare-earth material^{6, 7, 20}.

The mechanical constants like tetragonal modulus (C_S), Zener anisotropy ratio (A), Young's modulus (Y), isotropic shear modulus (G), Poisson's ratio (ν) and B/G ratio at room temperature are obtained by using SOECs values at room temperature given in Table 2. The expressions used for their calculations are given in our previous paper²⁸.

The Born criterion²⁹ $C_S = (C_{11} - C_{12})/2 > 0$, $B_T = (C_{11} + 2C_{12})/3 > 0$ and $C_{44} > 0$ for stability is satisfied for all these materials. Hence these materials are mechanically stable. The ratio of isotropic shear modulus to bulk modulus *i.e.*, G/B (toughness/fracture) is greater than 0.57, so the materials have brittle nature. The nature of bonding forces can be analysed from Poisson's ratio. For central forces, the value of Poisson's ratio should lie in region $0.25 < \nu < 0.5$. For the material considered in our study the value does not fall in the range which means that the forces are non central³⁰. The value of Young's modulus is greater for YS and hence YS is stiffer than other materials. Figure 1 shows the values of B , C_S and G for both materials. B , C_S and G were found highest for YS. This indicates that YS is the most stable materials among them.

Table 2 – Mechanical constants for YCh (Ch: S, Se, Te).

Material	C_S^*	G^*	A	Y	ν	B/G
YS	2.24	1.88	0.775	4.64	0.23	0.65
YSe	2.15	1.65	0.64	4.09	0.23	0.65
YTe	1.99	1.35	0.52	3.34	0.23	0.64

*(in units 10^{10}Nm^{-2})

Table 3 – Temperature dependent ultrasonic velocities (10^3ms^{-1})

Temp. (K)	YS			YSe			YTe		
	V_L	$^aV_{SI}$	$^bV_{S2}$	V_L	$^aV_{SI}$	$^bV_{S2}$	V_L	$^aV_{SI}$	$^bV_{S2}$
100	3.28	1.85	2.86	2.78	1.52	2.53	2.44	1.28	2.36
200	3.3	1.85	2.95	2.79	1.53	2.61	2.46	1.28	2.44
300	3.32	1.86	3.04	2.81	1.53	2.7	2.47	1.29	2.52
400	3.33	1.86	3.13	2.83	1.53	2.78	2.49	1.29	2.6
500	3.35	1.87	3.22	2.85	1.54	2.86	2.51	1.29	2.68

^ashear waves polarized along $\langle 001 \rangle$ direction; ^bshear waves polarized along $\langle \bar{1}10 \rangle$ direction

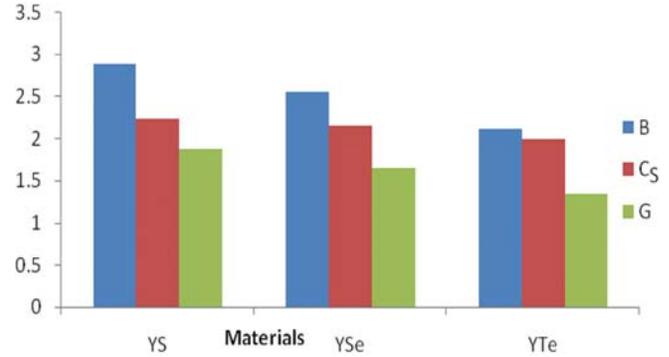


Fig. 1. B, C_S and G at room temperature

The computed values of ultrasonic velocities are shown in Table 3. The values of Debye average velocity, Debye temperature and Breazeale's non-linearity parameter at room temperature are shown in Table 4.

The value for ultrasonic velocity for YS is greater in comparison to YSe and YTe so propagation of sound waves is better in YS. The Debye temperature decreases with increase in atomic number and lattice constant.

Table 4 – V_D , θ_D and β of YCh at 300K

Material	$\langle 110 \rangle$		
	V_D	θ_D	β
YS	2.39	258.75	5.89
YSe	1.99	206.54	5.91
YTe	1.71	166.07	5.94

This kind of behaviour is seen in holmium mononictides⁶. The non-linearity parameter (β) is a function of ratio of SOECs. This parameter is presented in Table 4. β is highest for YTe. So we can say here that β is directly proportional to molecular weight of the material.

Temperature dependent thermal conductivity for YCh is calculated using the Eq. (8) and is shown in Fig. 2. The value of thermal conductivity is inversely proportional to temperature as well as molecular weight of the given materials as shown in Fig. 2.

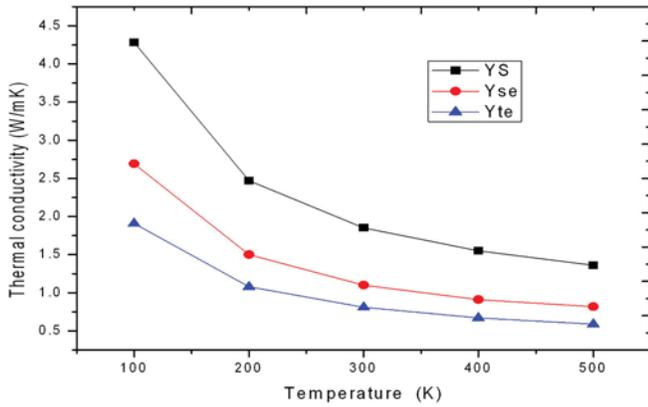


Fig. 2. Variation of thermal conductivity with temperature along $\langle 110 \rangle$ direction

The temperature dependent thermo-elastic loss and Akhieser loss (due to p-p interaction for longitudinal and shear waves) are visualized in Figs. 3-6. It is observed from Figs. 3-6 that the thermal loss is mainly depends on the thermal conductivity. So it has more or less trend as observed for thermal conductivity. The Akhieser loss

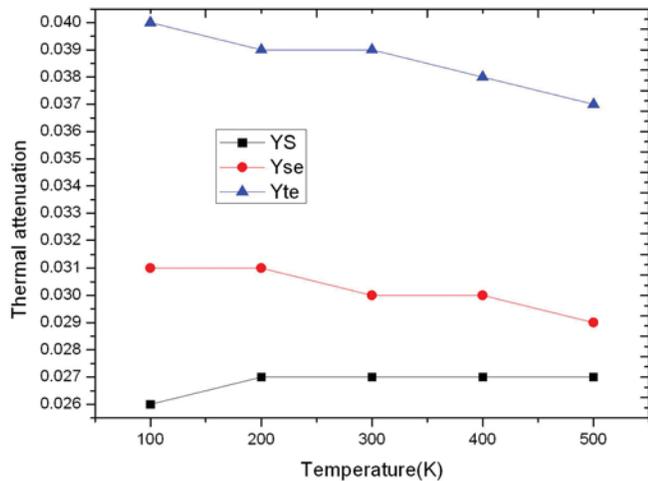


Fig. 3. Thermal attenuation [in unit of $10^{-16} \text{Nps}^2 \text{m}^{-1}$] with temperature along $\langle 110 \rangle$ direction

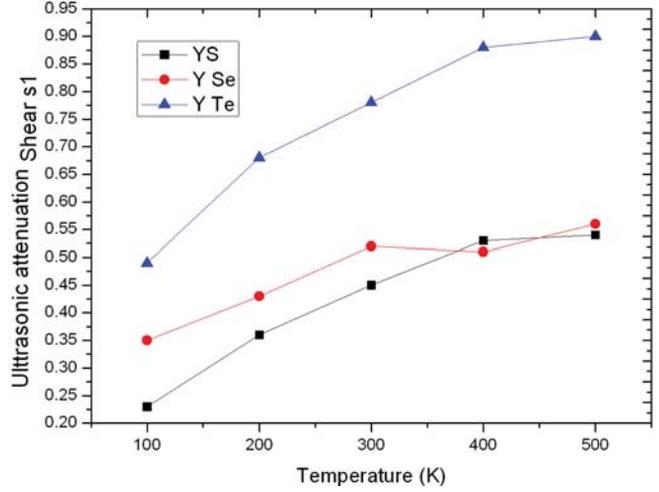


Fig. 4. Ultrasonic attenuation $\alpha/f^2_{\text{Akh, shear.S1}}$ with temperature along $\langle 110 \rangle$ direction [in unit of $10^{-16} \text{Nps}^2 \text{m}^{-1}$]

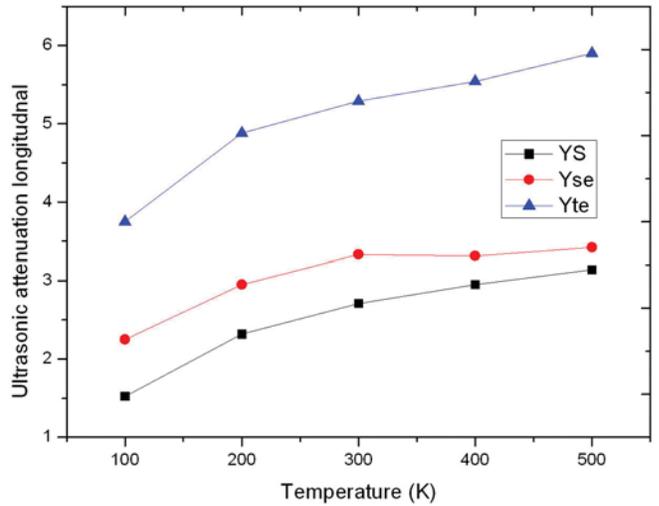


Fig. 5. Ultrasonic attenuation [in unit of $10^{-16} \text{Nps}^2 \text{m}^{-1}$] with temperature along $\langle 110 \rangle$ direction

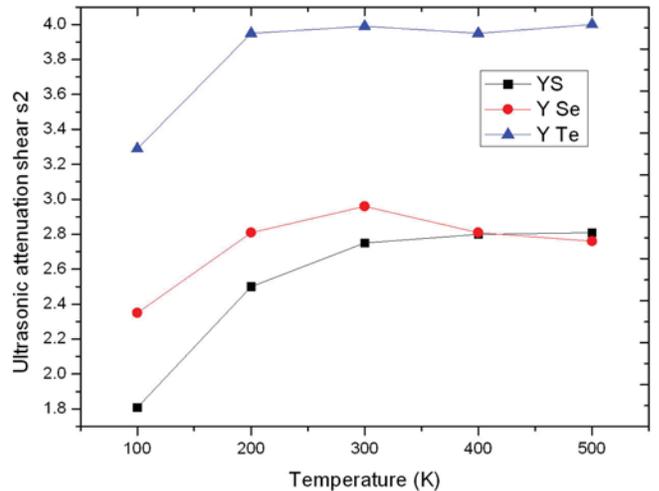


Fig. 6. Ultrasonic attenuation $\alpha/f^2_{\text{Akh, shear.S2}}$ with temperature along $\langle 110 \rangle$ direction [in unit of $10^{-16} \text{Nps}^2 \text{m}^{-1}$]

(loss due p-p interaction) increases with temperature along $\langle 110 \rangle$ direction. The loss due to p-p interaction has been affected by not only thermal conductivity but also many other factors such as energy density, density, acoustic coupling constants.

From Figs. 3-6, it is also noticeable that ultrasonic attenuation due to p-p interaction is predominant over thermo-elastic loss. This type of trend of ultrasonic loss is very similar to loss in case of monochalcogenides of lanthanum²³, lutetium³¹ and thulium³². The quantum of the thermal loss and Akhieser loss indicate that YCh have semiconducting behaviour.

Conclusions

We conclude following points on the basis of above discussion:

- The Coulomb and Born Mayer potential have been applied to calculate the higher order elastic constants successfully.
- The higher order elastic constants are higher for YS therefore mechanical properties of YS are better.
- According to Born criterion, these materials are stable as $B > 0$, $C_S > 0$ and $C_{44} > 0$.
- G/B values are greater than 0.57, so these materials are brittle in nature.
- The ultrasonic velocity is higher for YS among the chosen materials. So YS is better texture material.
- Breazeale's non-linearity parameter lies in the range from 0-16 which is typically the range of solids.
- The lowest attenuation is found in YS so the energy loss is lowest. Hence YS is most useful material for industrial purpose.

Hence these important discussed characteristics make yttrium monochalcogenides for possible under extreme condition. Such important feature would be very useful for improving the future performance of yttrium monochalcogenides and their futuristic applications.

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Ultrasonic study of acoustical parameters of dextran solution with 1(N) NaOH at different temperatures and concentrations

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The ultrasonic studies in solutions are great use in understanding the nature and strength of molecular interaction. The thermo-physical parameters like density, ultrasonic velocity and viscosity have been measured for dextran solution with NaOH at 303K, 308K, 313K, 318K and 323K at 9MHz frequency in different concentration of dextran solution. Using the experimental values of density, viscosity and ultrasonic velocity some of the acoustical parameters such as, acoustic impedance, adiabatic compressibility, intermolecular free length, relaxation time, Gibb's free energy have been calculated at constant frequency. The behavior of these parameters with composition of the solution has been discussed in terms of molecular interaction between the solute-solvent interaction and packing effects of solutes with solvent molecules.

Keywords: Dextran solution, ultrasonic velocity, acoustic impedance, adiabatic compressibility, intermolecular free length.

Introduction

In recent years ultrasonic technique has become a powerful tool in providing information regarding the molecular behaviour of liquids, polymer solutions and mixtures etc. and owing to its ability of characterizing physio-chemical behaviour of the medium. The ultrasonic velocity gives information about the bonding between the solute-solvent molecules and formation of complexes at various temperatures through molecular interactions¹⁻². In the present work, an attempt has been made to investigate the behavior of dextran solution with NaOH. Thermo-acoustic parameters such as acoustic impedance (Z), adiabatic compressibility (β), intermolecular free length (L_f), relaxation time (τ), Gibb's free energy (ΔG) of novel polymer dextran of molecular weight 70,000 at five different concentration *i.e.* 0.1%, 0.25%, 0.50%, 0.75% and 1% in solvent NaOH at five different temperature ranging from 303K to 323K at constant frequency of 9 MHz. have been measured. Dextran consists of α -D glucose units with a majority of α

(1 \rightarrow 6) glucosidic linkage between them. Dextran is a branched polysaccharide which is water soluble and is composed of α -D-glucopyranosyl residues. Dextran and their derivatives find wide applications in various industries, particularly in pharmaceutical sector³⁻⁵. Development in science and technology for non-destructive technique are spectacular and holds significant possibilities for more & more new applications in molecular structure, molecular interactions, medicines and underwater acoustics. Thermodynamics and acoustic studies of polymer solutions have attracted much attention of scientists⁶. These waves have many applications in various fields such as basic science, medical science, forensic science, space research *etc.* The previous studies had shown that the investigations of molecular interactions using ultrasonic wave⁷ provides valuable information regarding internal structure, molecular association. The variation in ultrasonic velocity gives information about the bonding between molecules and formation of complexes at various concentrations and temperatures through molecular interactions.

Materials and Method

In present study, the solute is Dextran of molecular weight 70,000 (Hi-media) and solvent is NaOH (Fisher scientific), both are of analytical reagent (AR) grade and are used as such throughout the experiments. The density of solvent and the solution are measured using a 25 ml specific gravity bottle with an accuracy of $\pm 0.1 \text{ K gm}^{-3}$ and calculated using standard equation. An Ostwald's viscometer was used for the viscosity measurement of polymer solution with accuracy 0.001 NSm^{-2} immersed in the temperature controlled water bath. The ultrasonic velocity in the polymer solution have been measured using an ultrasonic interferometer working at frequency 9 MHz with an overall accuracy of $\pm 0.1 \text{ ms}^{-1}$. All the precautions were taken to minimize the possible experimental error.

Theory

The data of density (ρ), viscosity (η) and ultrasonic velocity (U) has been used to determine other thermodynamic and acoustical properties by using the following standard equations;

- i. Acoustic impedance $Z = U\rho$
- ii. Adiabatic compressibility $\beta = \frac{1}{\rho u^2}$
- iii. Intermolecular free length $L_f = \frac{kT}{u\rho^{\frac{1}{2}}}$
- iv. Relaxation time $\tau = \frac{4}{3} \frac{\eta}{\rho u^2}$
- v. Gibb's free energy $\Delta G = kT \ln \frac{kT\tau}{h}$

Where symbols have their usual meanings.

Results and Discussion

A measure of how strongly molecules are held in polymer solution is their ultrasonic velocity, viscosity, density and their derived parameters such as acoustic impedance, adiabatic compressibility, intermolecular free length, relaxation time, and Gibb's free energy at constant frequency. Out of these some parameters are directly and some are inversely related to the strength of intermolecular forces that exist in polymer solution. Intermolecular forces may be long range or short range forces. Long range forces are dispersion forces and electrostatic induction. They occur when molecules come closer together causing a significant overlap of electron density having a specific geometry⁸ these are considered to be very important thermodynamic parameters. These parameters give information about how closed the solute-solvent molecules are held, freedom of motion, the amount of empty space in polymer solution and what types of forces (dipole-dipole, ion-dipole, ion-induced dipole and dipole-induced dipole) exist between solute-solvent molecules. The density, viscosity, ultrasonic

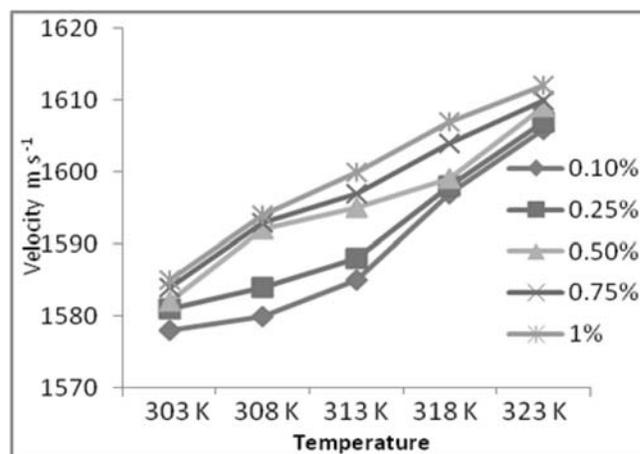


Fig. 1. Variation of velocity with temperature

Table 1 – Values of density (ρ) and viscosity (η) of dextran solution in 1(N) NaOH.

T Kelvin	Concentration									
	0.10%		0.25%		0.50%		0.75%		1%	
	ρ kg m ⁻³	$\eta \times 10^{-3}$ N s m ⁻²	ρ kg m ⁻³	$\eta \times 10^{-3}$ N s m ⁻²	ρ kg m ⁻³	$\eta \times 10^{-3}$ N s m ⁻²	ρ kg m ⁻³	$\eta \times 10^{-3}$ N s m ⁻²	ρ kg m ⁻³	$\eta \times 10^{-3}$ N s m ⁻²
303	1035.679	0.973	1036.075	0.982	1036.868	1.000	1037.264	1.027	1039.640	1.256
308	1033.667	0.869	1034.855	0.887	1035.647	0.904	1036.043	0.921	1039.212	1.126
313	1031.842	0.767	1032.634	0.800	1033.822	0.810	1034.218	0.835	1037.781	1.070
318	1028.238	0.730	1030.613	0.756	1031.008	0.765	1032.196	0.774	1035.758	0.989
323	1025.229	0.673	1027.206	0.682	1027.997	0.698	1029.578	0.723	1032.741	0.893

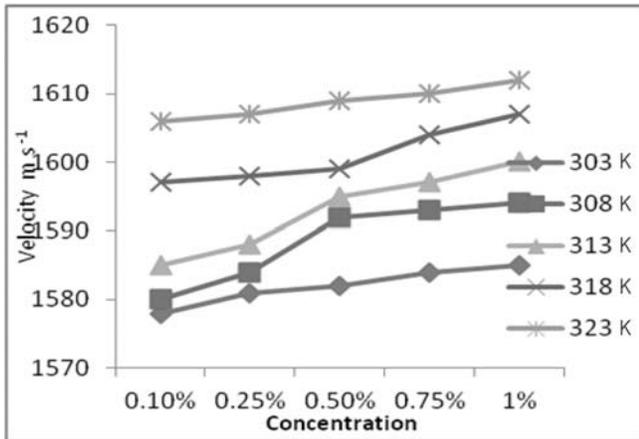


Fig. 2. Variation of velocity with concentration

velocity and acoustic impedance (Z) of dextran in 1(N) NaOH of different concentration are represented in Tables 1 and 2 at temperature 303K, 308K, 313K, 318K and 323K. From the experimental data, various acoustic and thermo dynamical parameters such as; acoustic

impedance (Z), adiabatic compressibility (β), intermolecular free length (L_f), relaxation time (τ), Gibb's free energy (ΔG) are represented in Tables 3 and 4.

Density is an important parameter with respect to buoyancy, purity and packaging. Density and viscosity decreases with increase in temperature indicates decrease in inter molecular forces due to increase in thermal energy of the system. This causes an increase in volume and hence decreases in density and viscosity. It indicates the decrease in solute-solvent and solvent-solvent interactions which results in a structure- breaking of the solvent. As density and viscosity of any solution or solvent are directly related to each other, the measured values show similar trend from the computed data given in Table-1. It is observed that ultrasonic velocity increases with increase in concentration (vol. %) of dextran in NaOH, indicating the increase in stiffness of the mixture and hence association. The increase suggests a structure-making capacity of polymers in solution. The solute

Table 2 – Values of ultrasonic velocity (U) and Acoustic impedance (Z) of dextran solution in 1(N) NaOH.

T (kelvin)	Ultrasonic velocity (U) m/s					Acoustic impedance (Z) 10^6 kg·m ² ·s ⁻¹				
	0.10%	0.25%	0.50%	0.75%	1%	0.10%	0.25%	0.50%	0.75%	1%
303	1578	1581	1582	1584	1585	1.634	1.638	1.640	1.643	1.648
308	1580	1584	1592	1593	1594	1.633	1.639	1.649	1.650	1.657
313	1585	1588	1595	1597	1600	1.635	1.640	1.649	1.652	1.660
318	1597	1598	1599	1604	1607	1.642	1.647	1.649	1.656	1.664
323	1606	1607	1609	1610	1612	1.647	1.651	1.654	1.658	1.665

Table 3 – Values of adiabatic compressibility and acoustic impedance of dextran solution in 1(N) NaOH.

T (kelvin)	Adiabatic Compressibility (β)(10^{-10} N ⁻¹ .m ²)					Intermolecular free length (L_f) 10^{-10} m				
	0.10%	0.25%	0.50%	0.75%	1%	0.10%	0.25%	0.50%	0.75%	1%
303	3.878	3.861	3.854	3.842	3.829	3.907	3.899	3.895	3.889	3.882
308	3.875	3.851	3.810	3.804	3.787	3.940	3.928	3.906	3.903	3.895
313	3.858	3.840	3.802	3.791	3.764	3.965	3.956	3.936	3.930	3.916
318	3.813	3.800	3.792	3.766	3.739	3.976	3.968	3.964	3.951	3.936
323	3.782	3.770	3.757	3.747	3.726	3.993	3.986	3.980	3.974	3.963

Table 4 – Values of relaxation time and Gibb's free energy (ΔG) of dextran solution in 1(N) NaOH.

T (kelvin)	Relaxation time (τ)(10^{-13} Sec.)					Gibb's free energy(ΔG) 10^{-20} kJ·mol ⁻¹				
	0.10%	0.25%	0.50%	0.75%	1%	0.10%	0.25%	0.50%	0.75%	1%
303	5.030	5.056	5.139	6.043	6.411	209.951	210.876	213.833	218.053	254.002
308	4.490	4.553	4.593	5.265	5.684	195.453	198.037	199.628	202.785	239.001
313	3.945	4.099	4.105	4.866	5.369	177.338	184.532	184.806	189.983	235.213
318	3.713	3.832	3.867	4.560	4.931	171.684	177.697	179.427	180.325	225.740
323	3.392	3.427	3.498	4.104	4.436	159.857	161.881	165.851	172.079	211.836

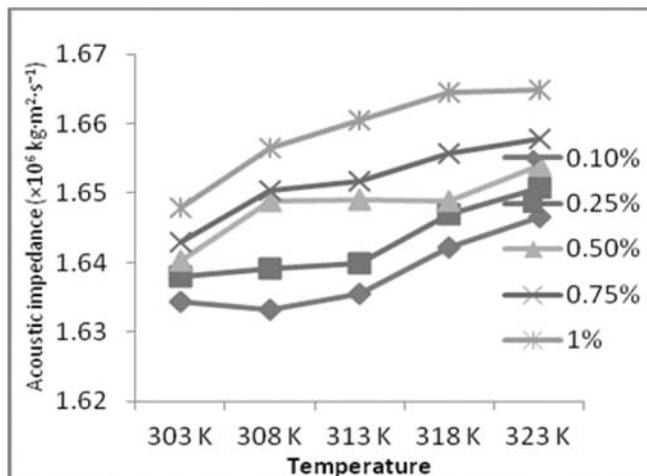


Fig. 3. Variation of acoustic impedance with temperature

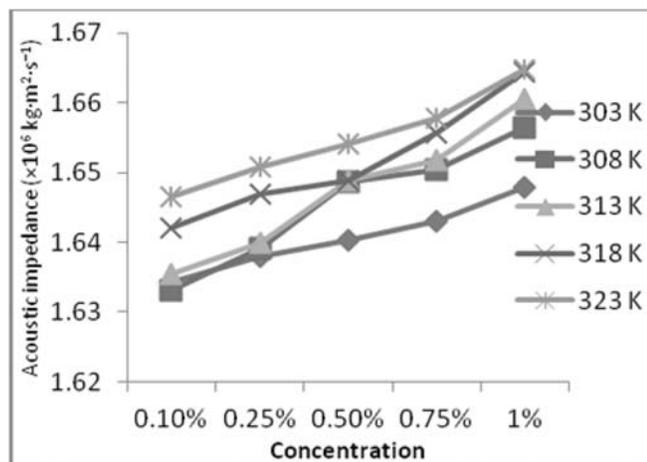


Fig. 4. Variation of acoustic impedance with concentration.

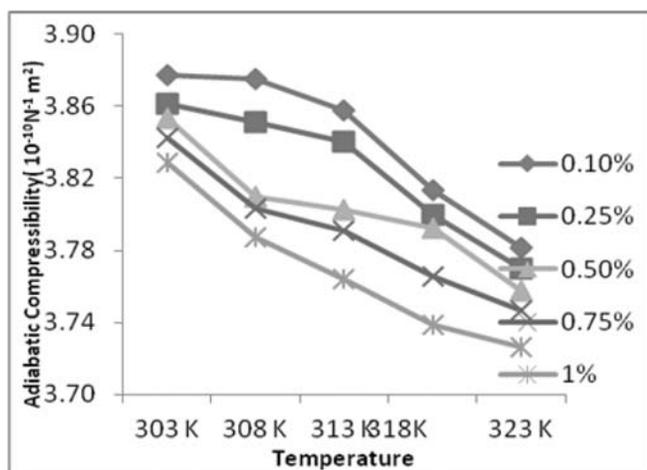


Fig. 5. Variation of adiabatic compressibility with temperature

occupy the interstitial space of solvent and tend to break the ordered state of solvent due to its self-association. But With increase in temperature there occurs a structural

rearrangement as a result of solvation leading to a comparatively more ordered state⁹. The acoustic impedance value also increases as shown in Table 2 which indicates the interaction between the solute and solvent molecules. This is due to increase in pressure and cohesive energy of the system because of strong interaction¹⁰. Figure 6 contains the plots of adiabatic compressibility versus concentration. It is observed that adiabatic compressibility decreases with increase in concentration (vol. %) of Dextran in NaOH indicating strong intermolecular interaction between Dextran in NaOH which also shows associating tendency of molecules. This is because of the fact that dipole-dipole interaction of pure Dextran in NaOH. Adiabatic compressibility decreases with increase in temperature. This is due to the association taking place between the molecules. With the increase in temperature the force of attraction between the molecules decreases hence they move apart from each other so compressibility decreases.

Intermolecular free length (L_f) depends on the intermolecular attractive forces. As concentration increases, number of ions or molecules increase in a given volume leading to increase in attractive forces hence decrease in the gap (intermolecular free length) between two species¹¹. Also, the decrease in compressibility brings the molecules to a closer packing resulting in decrease in intermolecular free length. The variation of intermolecular free length with concentration is shown in Fig. 8. Inter molecular free length increases (Fig. 7) with increase in temperature. As the temperature increases it leads to the less order structured and more spacing between the molecules due to increase in thermal

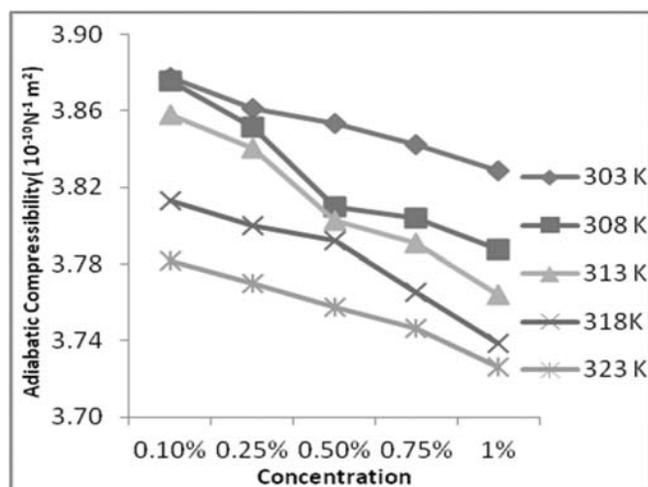


Fig. 6. Variation of adiabatic compressibility with concentration

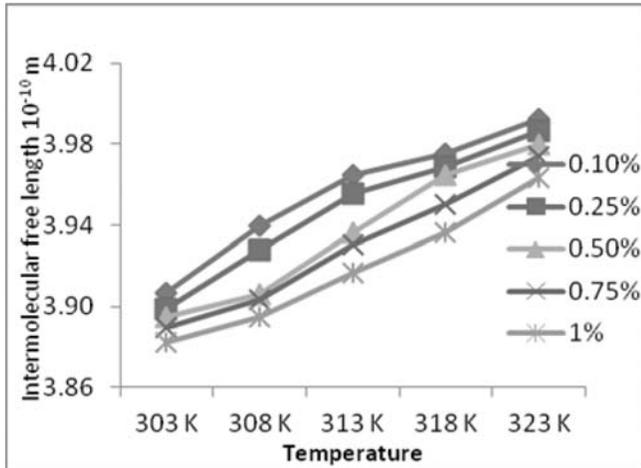


Fig. 7. Variation of intermolecular free length with temperature

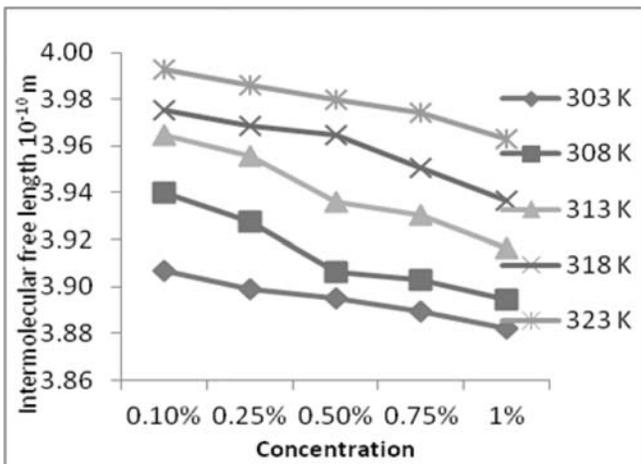


Fig. 8. Variation of intermolecular free length with concentration

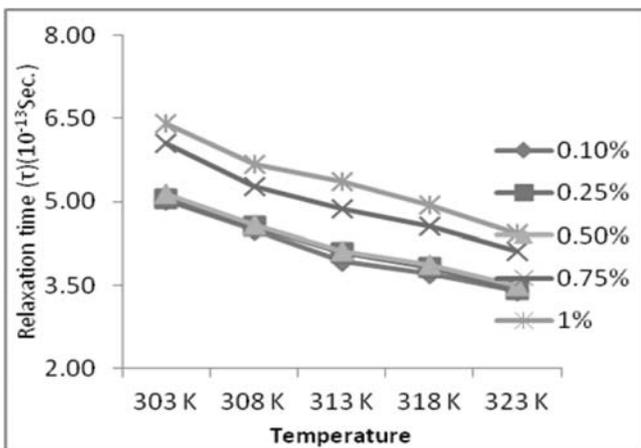


Fig. 9. Variation of relaxation time with with temperature

energy of the system which increases in volume expansion and hence increase in inter molecular free length. With increase in temperature excitation energy increases and hence relaxation time decreases. Increase in relaxation time with increase in concentration indicates (Fig. 10) that the solution is highly ordered due to excellent hydration. It is observed that Gibb's free energy $\Delta(G)$ increases with increase in concentration. This indicates that solution is highly ordered due to strong association among the solute and solvent molecules. The increase in Gibb's free energy with concentration suggests shorter time for rearrangement of the solute molecules in the solution. Viscous relaxation time and Gibbs free energy both decrease as temperature increases as shown Fig. 9 and Fig. 11 respectively. Further as the kinetic energy of the molecule increases, it takes long time for rearrangement of molecule and this suggests a decrease in Gibb's free energy. This behaviour suggests the formation of more compact structure, possible due to dipole-dipole interaction (hydrogen bonding) at the sites on the hydroxyl group (OH) of solute and water molecules¹².

Conclusions

From the experimentally measured parameters (*i.e.* density, viscosity and ultrasonic velocity) of the solution of dextran in¹ NaOH at different concentrations and temperatures various thermo-acoustic parameters like acoustic impedance, adiabatic compressibility, intermolecular free length, relaxation time, Gibb's free energy, have been calculated at 9 MHz frequency. The results show that the specific solute-solvent interactions play an important role for explaining acoustic parameters.

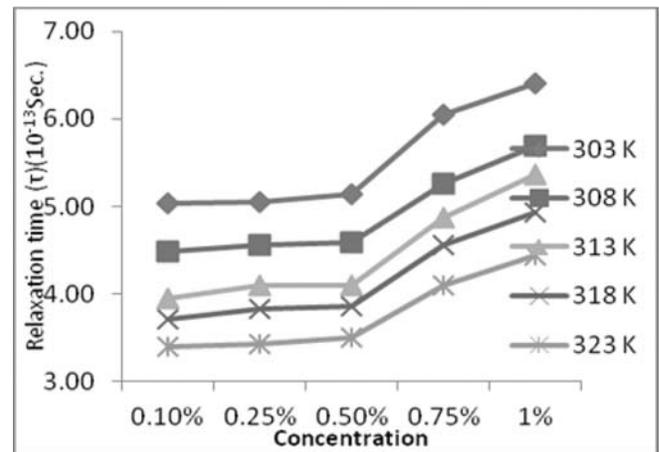


Fig. 10. Variation of relaxation time with concentration

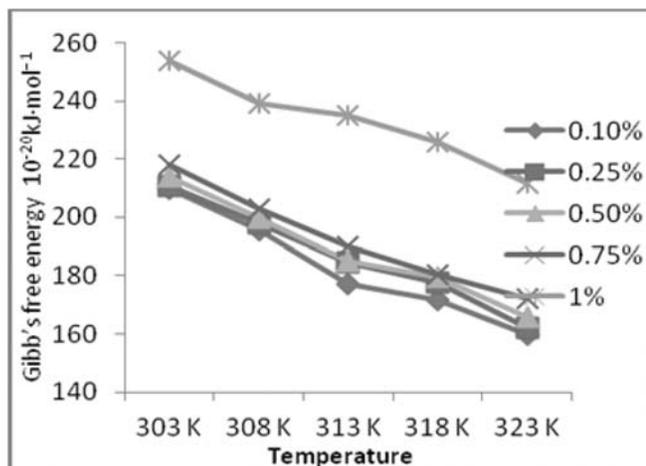


Fig. 11. Variation of Gibb's free energy with temperature

However, any deviation from the usual behaviour is due to characteristic structural changes in the respective system.

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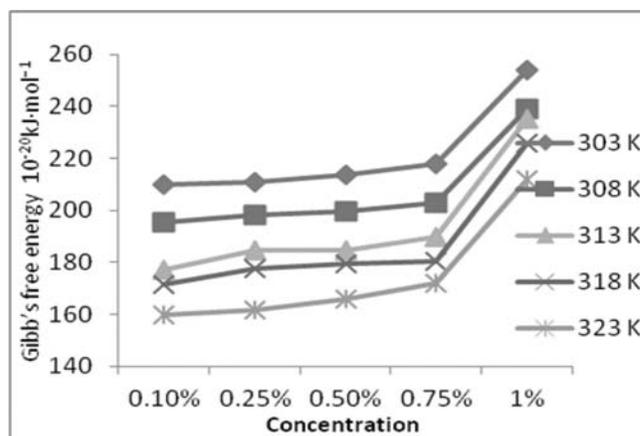


Fig. 12. Variation of Gibb's free energy'with concentration

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Ultrasonic study of aqueous solution of cellulose with NaOH for surface modification of natural fiber

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The important issue in composite technology is the interfacial strength between the fiber and matrix. The strong bonding in the interfacial region is essential for achieving high mechanical performances of biocomposites. Therefore, a number of chemical and physical treatment studies on a variety of natural fibers have been devoted to understand and enhance the interfacial adhesion between the natural fibers and the polymer matrix and to further improve the composite properties. In the present study, sodium hydroxide was independently used as fiber surface treatment media. Ultrasonic technique can be utilized as a dynamic treatment to understand the basic mechanism in chemical treatment of natural fiber. Ultrasonic velocity, and density have been measured in the aqueous solutions of Cellulose with sodium hydroxide, with a view to understand the nature of interaction between the cellulose and sodium hydroxide at temperature 303K. The acoustical parameters such as adiabatic compressibility, intermolecular free length, acoustic impedance are calculated. These parameters provide valuable information regarding achieving of high mechanical performances of natural fiber. The SEM and FTIR data of untreated and treated date palm fiber clearly shows the improvement of surface of date palm leaf.

Keywords: Natural fiber, cellulose, surface treatment, ultrasonic wave, acoustic parameters.

Introduction

The incorporation of natural fibres into a matrix is often associated with poor fibre compatibility as their cellulose surface is covered by the hemicelluloses and lignin constituents. Hemicellulose and lignin act as a weak boundary layer between the cellulose (elementary fibre) and the matrix. Due to the presence of weak boundary layer at the fibre matrix interface, the stress distribution capacity throughout the composite area is reduced. To obtain a satisfactory performance of the composite, it is necessary to remove the weak boundary layers from the elementary fibres. A weak boundary layer can be removed by dissolving hemicelluloses and lignin coverings through different chemical treatments of the fibre. The use of chemicals for surface modification of natural fibers in trial basis like 5%, 10%, 15% *etc.* some times causes the disruptive effect on the fiber surface and also in composite fabrication. Thus to

avoid such type of difficulties in fiber surface modification and composite fabrication it is very essential to know an optimised concentration of each chemicals. The treatment of natural fibres by sodium hydroxide (NaOH) is being widely used to modify fibre structure. Natural fibre absorbs moisture due to the presence of hydroxyl groups in the amorphous region of cellulose, hemicelluloses and lignin constituents. However, too high of alkali concentration can cause an excess removal of covering materials from the cellulose surface, which results in weakening or damage to the fibre structure. It is important to select a treatment condition for a particular natural fibre to analyse the treatment effects on the fibre structure and the morphological changes. These changes need to be systematically explored through the compatibility with the matrix and their composites 'mechanical property analysis. Being ultrasonic wave a high frequency irradiation can penetrates into different regions of a multiphase system in the atomic

level which is inaccessible when using other method. This mechanism is called ultrasonic leaching which enables solvents to more readily enter the interior of the pores of the materials and increases the reactive sites and moieties for the reaction of fibers with the matrix.

Experimental

Materials and methods

All chemicals used in this present work were of analytical reagent (AR) grade of minimum assay of 99.9% obtained, SD chemicals, India. Double distilled water was used to prepare the stock solution. Required amount of water and cellulose was taken to prepare the composition of 0.4 M of binary mixtures and 1 N aqueous solution of NaOH was prepared. The different concentrations of aqueous solution of NaOH were dissolved in 0.4 M of aqueous cellulose. For this different concentration, ultrasonic velocities of solutions were measured using a single frequency continuous wave ultrasonic interferometer to an accuracy of $\pm 0.05\%$ at a frequency of 2 MHz at 303 K. The temperature of the samples was maintained constant to an accuracy of ± 0.1 K using thermostatically controlled digital water bath. The densities of the solutions was measured using a specific gravity bottle with an accuracy of ± 0.01 kg m⁻³.

Computed parameters

The different acoustical parameter such as adiabatic compressibility (β), intermolecular free length (L_f), acoustic impedance (Z), has been calculated using the measured data of ultrasonic velocity and density of the medium using the Newton-Laplace equation.

$$\text{Adiabatic compressibility } \beta = 1/\rho.C^2 \quad (1)$$

$$\text{Intermolecular free length, } L_f = k.\beta^{1/2} \quad (2)$$

$$\text{Acoustic impedance, } Z = \rho.C \quad (3)$$

The constant k is temperature dependent which is given as $[93.875 + (0.375T)] \times 10^{-8}$ and "T" being the absolute temperature.

Characterisation of untreated and treated NaOH date palm leaf fiber with SEM and FTIR

Microscopic examinations were carried out using a HITACHI SU3500 scanning electron microscope (SEM). All specimens were sputtered with 10 nm layer of gold prior to SEM observations. Several

samples were examined to ascertain the observed phenomena. The FTIR spectra of raw and surface treated fibers were recorded in a Perkin-Elmer 2000 spectrophotometer in the form of KBr Pellets of finely ground fibers samples. The injection molded specimens were conditioned at 30°C at the laboratory atmosphere for a minimum of three days.

Results and Discussion

The values of density and ultrasonic velocity of aqueous Cellulose in the presence of aqueous NaOH at 303 K are presented graphically. By using ultrasonic velocity and density, various acoustical parameters like adiabatic compressibility (β), Intermolecular free length (L_f) and acoustic impedance (Z), were calculated using the acoustical relations. The variation in ultrasonic velocity as shown in Fig. 1 in any solution generally indicates molecular association in it. The ultrasonic velocity decreases suddenly when the NaOH is added to the aqueous cellulose solution.

The decrease of velocity in addition of NaOH is an

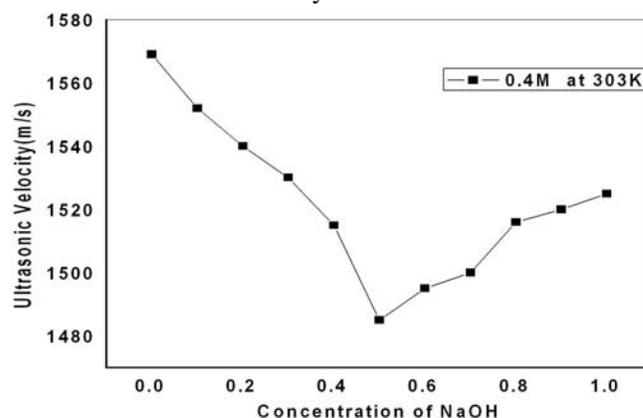


Fig. 1. Variation of ultrasonic velocity

indicative for the influence of metal ions on the aqueous cellulose solution which strengthens the intermolecular force³. Aqueous NaOH solution being ionic in nature (as shown in Fig. 2), the ionic field has a great influence on the cellulose. Hence the interaction is favoured between cellulose polymer and ion which makes the solution a good solvent medium for the ions of NaOH. This results in the sudden decrease of velocity on addition of aqueous NaOH to cellulose solutions. The increase in ultrasonic velocity value at 0.5% of cellulose solution with aqueous NaOH solutions may be attributed to overall increase of cohesion brought about by the solute-solute, solute-solvent and solvent solvent interaction in

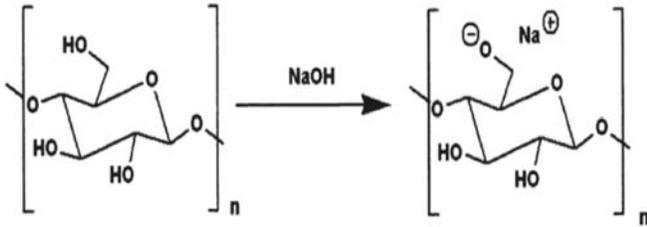


Fig. 2. Reaction of cellulose with NaOH

the solution.

The decrease of velocity in addition of NaOH is an indicative for the influence of metal ions on the aqueous cellulose solution which strengthens the intermolecular force³. Aqueous NaOH solution being ionic in nature (as shown in Fig. 2), the ionic field has a great influence on the cellulose. Hence the interaction is favoured between cellulose polymer and ion which makes the solution a good solvent medium for the ions of NaOH. This results in the sudden decrease of velocity on addition of aqueous NaOH to cellulose solutions. The increase in ultrasonic velocity value at 0.5% of cellulose solution with aqueous NaOH solutions may be attributed to overall increase of cohesion brought about by the solute-solute, solute-solvent and solvent solvent interaction in the solution.

The increase in adiabatic compressibility (β) and intermolecular free length clearly indicates a break in the cellulose water bonding which reduces the number of water molecules and decrease in β is due to the increase in electrostriction compression of solvent around the molecules as shown in Figs. 3 and 4.

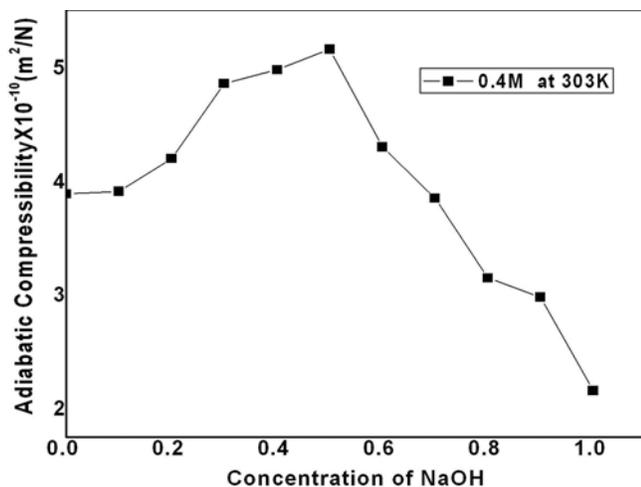


Fig. 3. Variation of adiabatic compressibility

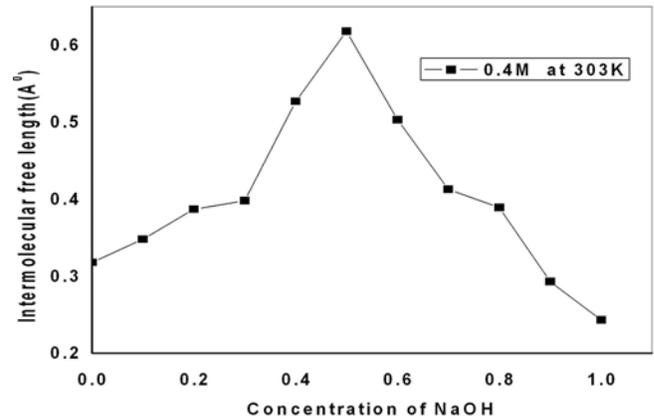


Fig. 4. Variation of intermolecular free length

The decrease in adiabatic compressibility is attributed to the influence of the electrostatic field of the ions on the surrounding solvent molecules⁴. The decrease in compressibility implies that there is enhanced molecular association in these systems upon increase in solute content, as the new entities (formed due to molecular association) become compact and less compressible. These also suggest that the compressibility of the solution will be lesser than that of solvent. As a result, solute will have mobility and have more probability of contacting solvent molecules. This may enhance the interactions between solute and solvent molecules⁵. The decrease in free length with increase in solvent concentration indicates that there is a significant interaction between the solute and solvent molecules, suggesting a structure promoting behavior on the addition of solute. The acoustic impedance (Z) decreases with decreasing concentration of salt solutions suggesting that the ion-solvent interaction decreases as shown in Fig. 5. The increasing trend in these parameters suggests the strengthening of interaction among the component⁶.

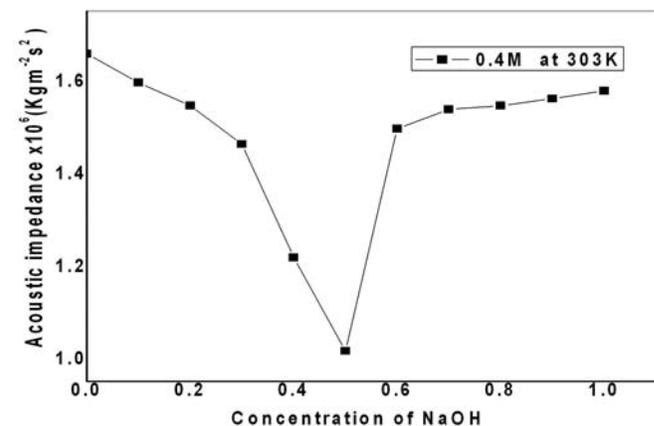
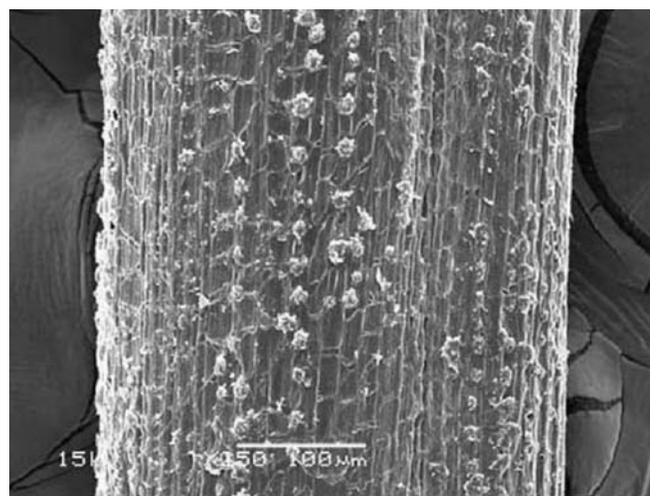
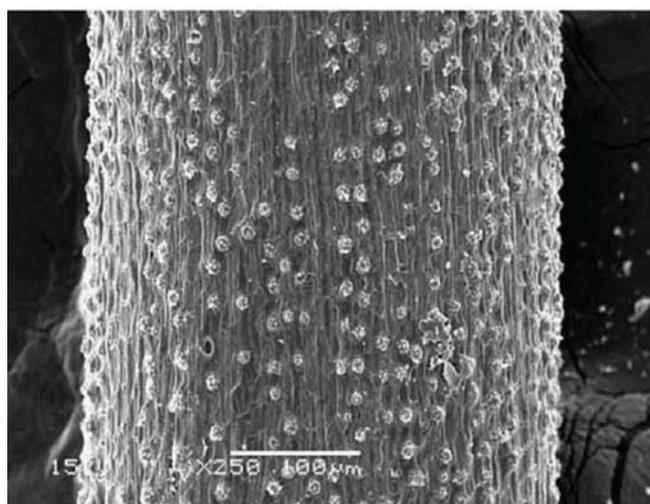


Fig. 5. Variation of acoustic impedance

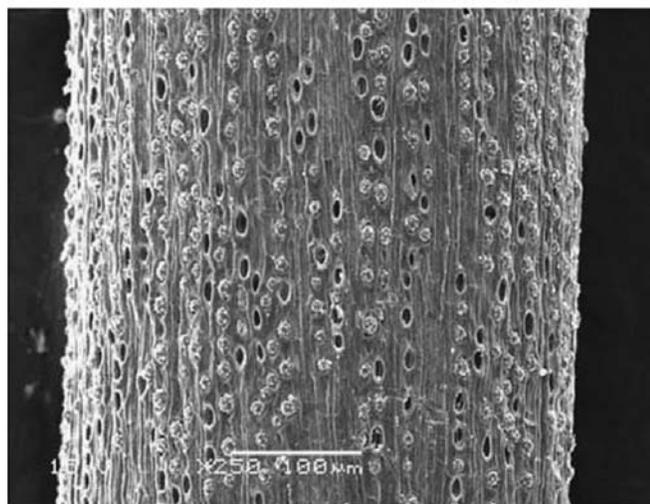
The SEM micrographs taken from the fibers surface are shown in Fig. 6. It can be seen from the images that



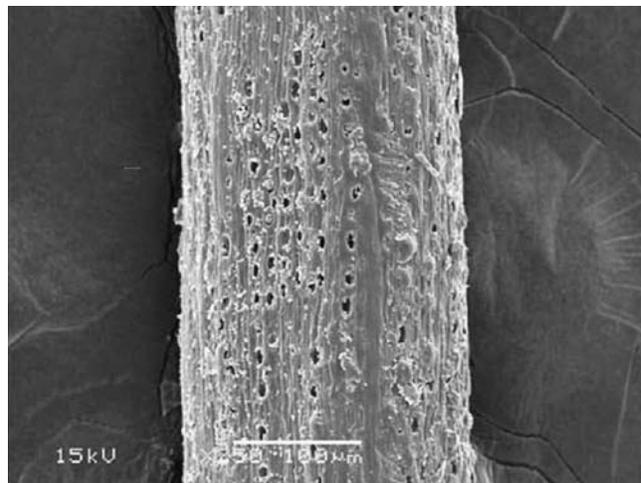
(a)



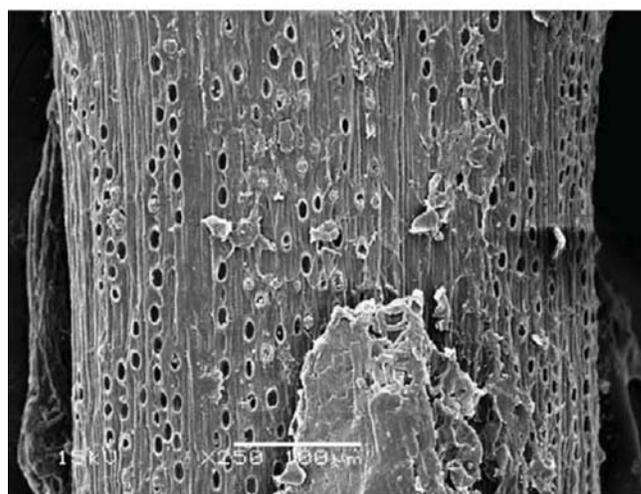
(b)



(c)



(d)



(e)

Fig. 6. SEM for DPLF that treated with (a) 0.2%, (b) 0.4%, (c) 0.5%, (d) 0.8% and (e) 1.5 % NaOH

the surface treatment process gently cleaned the fiber's surface without showing any indication of fiber damage. Alkaline treatment has two effects on the fiber: (1) it increases surface roughness resulting in better mechanical interlocking; and (2) it increases the amount of cellulose exposed on the fiber surface, thus increasing the number of possible reaction sites⁷.

The FTIR spectra of the alkali treated and untreated fibers is shown in Fig. 7. The peak occurring at around 3500 cm^{-1} corresponds to hydrogen bonded O-H stretching⁸ and the reduction in the peaks intensity could be attributed to the reduced number of OH groups from the fibers surface, which resulted in higher hydrophobic character in the fibers. The peak at about 2900 cm^{-1} results from CH stretching vibration. The absorption

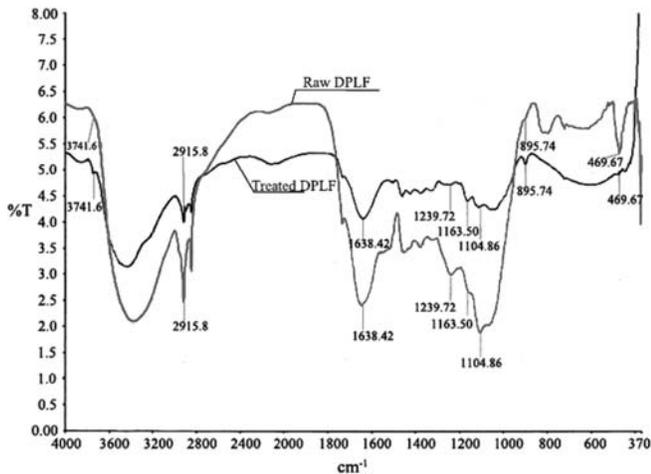


Fig. 7. FTIR spectra of treated and untreated date palm leaf fiber

band in the region of about 1638 cm^{-1} attributed to the carbonyl group (C=O) stretching. The reduction in the absorption of carbonyl region could be attributed to the removal of hemicelluloses during alkaline treatment⁸. The intensity at 1375 cm^{-1} band is attributed to bending vibration of CH_3 group.

Conclusions

The study of acoustic parameter in mixture of cellulose and aqueous solution of NaOH indicates that here is solute-solvent interaction. The non-linearity in acoustic parameters confirms the presence of solute-solvent, ion-ion, dipole dipole, ion-solvent interactions. The observed molecular interaction, complex formation, hydrogen bond formation are responsible for the hetero-molecular interaction in the liquid system. The variation of ultrasonic velocity and other parameters clearly indicates that interaction of ultrasonic wave with aqueous solution of cellulose and NaOH. The solute that increases the ultrasonic velocity is structure maker. This solute-solvent interaction increases the surface roughness resulting in better mechanical interlocking; increases the amount of cellulose exposed on the fiber surface, and increases the number of possible reaction sites by removing lignin. The image of SEM and FTIR spectra clearly indicates the conversion of hydrophilic nature into hydrophobic. The removal/stretching of O-H, CH part from the hemicellulose of date palm fiber is possible due to treatment

of NaOH. From the result analysis it is observed that conc. of NaOH is very effective from 0.5% to maximum 1%. The SEM image clearly indicates that the use of more NaOH solution may damage the fiber surface. This is also clearly observed from the variation of ultrasonic velocity and other supporting acoustic parameters.

Acknowledgements

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Effect of molecular structure of lubricating oil on sound velocity and bulk modulus

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Theoretical computation of sound velocity and their bulk modulus for many lubricating oils having various applications in machinery and daily lives at different ranges of temperature over the entire concentration range has been done from the measured data of Mia and Ohno. An attempt has also been envisaged to predict the molecular interactions and molecular structure involved therein and also to establish relationship among sound velocity, surface tension, adiabatic compressibility and their bulk modulus. It is found that theoretical results for sound velocity agreed well within the experimental precision when compared with experimental data. These properties are helpful in predicting the group of the lubricating oil of which they belong.

Keywords: Lubricating oil, surface tension, sound velocity, bulk modulus, molecular interactions.

Introduction

The branch of science and technology concerned with interacting surfaces in relative motion and with associated matters as friction, wear, lubrication and the design of bearing, is known as tribology. Common tribological components which are used in industrial applications include sliding contact and rolling contact bearings, seals, gears, cams and tappets, piston rings, electrical brushes and cutting and forming tools. Some of the other common industrial applications include material processing, internal combustion engines for automotive applications, gas turbine engines for aerospace applications, railroads and magnetic storage devices. For a desired performance and life of a component, its friction and wear needs to be minimized or optimized for a given application. Relevant friction and wear mechanisms are dependent upon the device and the operating condition.

The term lubricating oils is generally used to include all those classes of lubricating materials that are applied as fluids¹. Lubricants are functional materials in the mechanical system². A lubricating oil or lubricant is any substance used to separate two surfaces in relative motion which can be readily sheared while adhering the surfaces. Mainly,

lubricating oils are characterized by their viscosity, but other properties are also important. There are many kinds of lubricating oil. The most used lubricants are mineral or synthetic lubricants. Perfluoropolyether (PFPE) fluids are another type of lubricating oil used on magnetic recording media, aerospace industry and satellite instrument satisfactorily³⁻⁴. Recently these oils have been used as hydraulic fluids, high temperature liquid lubricants in turbine engine⁵ and the base oils of high-temperature greases. Sound velocity is directly related to the molecular structure and the properties such as density, bulk modulus, surface tension etc. which are related with molecular structure.

In this study, lubricating oils were considered as a group basis. There are many group of lubricating oil. Here the groups are considered on the basis of the molecular structure like traction oil (SN32, SN100 and CVTF), polyalphaolefin oil (PAO32, PAO68), paraffinic mineral oil (P60N, P150N, P500N, PBSN), perfluoropolyether oil (Fomblin, Demnum and Krytox), and glycerol. The tested lubricating oils and their physical properties are available in the literature. In this work, we emphasize on the bulk modulus, rather than the other parameters. Bulk modulus is related to the intermolecular force and the high-

pressure physical properties, and also depends on the free volume.

According to chemical structure, traction oils are naphthenic hydrocarbon, polyalphaolefin oils (synthetic branched hydrocarbon) and paraffinic mineral oils (long chain hydrocarbon). Perfluoropolyether and glycerol consists of different molecular structure where as PFPE consists of Fluorine with carbon bonding and glycerol has hydroxyl group. The relation between low temperature fluidity and the adiabatic bulk modulus of lubricating oil also exhibited the dependency on the molecular structure.

The property, density and surface tension are related to the molecular behavior of any substance. Adiabatic bulk modulus, K , of a substance essentially measures the uniform compression. It may also be defined that as the pressure increases, volume decrease relatively. This important property related to the molecular structure was calculated from the measured sound velocity. Sound velocity, density, bulk modulus, surface tension are directly related to the molecular structure.

Another important property of liquid is surface tension. It is a measurement of the cohesive energy present at an interface. The molecules of a liquid attract each other with an equal attractive force in all directions which balance the interactions of a molecule in the bulk of a liquid. There are many relations between the surface tension and other physical and chemical properties⁶. Macleod found that the fourth root of surface tension, divided by the density difference in the liquid and gas phase, is independent of temperature⁷,

$$\gamma^{1/4} / (\rho_L - \rho_G) = \text{constant.} \quad (1)$$

where γ is the surface tension of lubricating oil, ρ_L and

ρ_G refer to the densities of the lubricating oil in liquid and the gas phase. ρ_G can ordinarily be neglected. Finally Sound velocity of the sample oils were compared with the experimental findings. Here, sound velocity is calculated from the well tested relation of Auerbach⁸ as;

$$U = \left(\frac{\gamma}{6.3 \times 10^{-4} \rho} \right)^{2/3} \quad (2)$$

where γ is the surface tension and ρ refer to the density of the lubricating oil.

Results and Discussion

In the present work, experimental results of surface tension and viscosity are taken from the work of Mia and Ohno⁹. The experimental data of sound velocity and density were used to calculate the adiabatic compressibility and bulk modulus of the lubricating oil by Laplace¹⁰, then Wood¹¹ relation;

$$U = 1/(\beta\rho)^{0.5} \quad (3)$$

and adiabatic bulk modulus,

$$K = 1/\beta \quad (4)$$

A care full perusal of Table 1 indicates that sound velocity is proportional to its bulk modulus.

Glycerol has higher bulk modulus and it's sound velocity is also superior at measured temperature because hydrogen bond of glycerol shows greater intermolecular force with high bulk modulus. On the other hand perfluoro-polyether oils have low bulk modulus and the value of sound velocity in them are low. The reason is that, PFPE has higher free volume at testing temperature and low intermolecular force due to its fluorine bond. Table also shows the linear relation between the adiabatic bulk modulus and the sound velocity of oils with temperature. Here the relation between sound velocity and other properties are linear as evident in the Table 1.

Table 1 – Temperature (T), density (ρ), surface tension (γ), adiabatic bulk modulus (K), theoretical (U_{Theo}) and experimental sound velocity (U_{exp}) and percent error (%) of various lubricating oils.

Oil	T °C	ρ kg/m ³	γ mN/m	K GPa	U_{Theo} m/s	U_{exp} m/s	Error %
SN32	0	920.6	28.69	2.52	1488	1652	9.9
	20	904.0	26.40	2.11	1433	1529	6.3
	40	887.4	24.24	1.87	1378	1453	5.2
SN100	10	926.5	30.94	2.72	1549	1631	5.0
	20	918.2	29.23	2.31	1507	1588	5.1
	40	900.4	25.79	1.95	1417	1472	3.7

CVTF	0	971.1	32.72	2.46	1557	1586	1.8
	20	952.6	29.94	2.05	1496	1511	1.0
	40	933.5	27.27	1.93	1433	1437	0.3
P60N	-20	888.3	26.09	1.89	1438	1572	8.5
	0	871.2	24.87	1.83	1414	1511	6.4
	20	854.1	23.69	1.75	1390	1443	3.7
	40	837.0	22.55	1.57	1367	1370	0.2
P150N	0	874.2	30.07	1.86	1576	1549	-1.8
	20	861.0	28.10	1.77	1529	1479	-3.4
	40	847.8	26.23	1.68	1482	1408	-5.3
P500N	0	881.4	33.90	1.91	1682	1556	-8.1
	20	867.7	31.85	1.84	1637	1500	-9.1
	40	853.9	29.89	1.75	1592	1432	-11.2
PBSN	10	883.1	32.36	1.93	1635	1602	-2.1
	20	876.4	31.05	1.89	1603	1565	-2.5
	40	862.9	28.53	1.83	1540	1457	-5.7
	50	856.2	27.34	1.74	1509	1425	-5.9
	60	849.4	26.17	1.71	1478	1392	-6.2
PAO32	0	842.2	23.69	1.89	1402	1520	7.7
	20	825.7	22.63	1.74	1381	1451	4.9
	40	809.3	21.61	1.55	1360	1382	1.6
PAO68	0	848.6	29.50	1.84	1586	1534	-3.4
	20	832.3	25.95	1.77	1488	1465	-1.6
	40	816.0	22.73	1.59	1394	1395	0.1
Fomblin	-10	1907.4	18.76	1.33	761	821	7.3
	0	1884.9	18.52	1.12	761	795	4.2
	20	1839.8	18.04	1.02	760	743	-2.2
	40	1794.7	17.57	0.86	759	693	-9.5
	60	1749.7	17.11	0.84	759	647	-17.2
Demnum	-10	1956.2	20.87	1.32	799	851	6.2
	0	1930.5	20.05	1.13	786	823	4.5
	20	1879.2	18.47	1.09	761	761	0.0
	40	1827.9	16.99	0.93	737	712	-3.4
	60	1776.5	15.60	0.81	713	669	-6.5
Krytox	10	1930.0	18.14	1.23	742	788	5.9
	20	1906.2	17.57	1.11	733	763	3.9
	40	1858.7	16.47	0.98	717	726	1.3
	60	1811.3	15.43	0.83	700	673	-4.1
Glycerol	-5	1284.5	61.45	4.72	1911	1960	2.5
	0	1280.1	61.07	4.68	1908	1941	1.7
	20	1262.1	59.55	4.40	1896	1880	-0.8
	40	1244.2	58.07	4.21	1884	1841	-2.3

The relation between density and sound velocity is also linear with temperature.

Among them, paraffinic mineral oils is chain like hydrocarbon with single bond between the carbons. These molecules are linear whereas PAO is similar to

paraffinic mineral oils except that they contain one or more double bonds between carbon atoms with branch carbon bonding. Traction oils are naphthenic hydrocarbon, which contains ring like molecule also known as cyclo-paraffin. Ring like molecules are stronger

than the chain like molecule and bulk modulus and density is slightly higher at the same condition. Therefore, sound velocity is also slightly higher.

Sound velocity is an important property of lubricant. Since it is related to molecular structure and affect the molecular structure of lubricant. Sound velocity decreases with the increase of temperature and increases with the increase of bulk modulus. So, sound velocity of lubricating oils can indicates roughly the molecular structure of that lubricating oil. Kagathara and Parsania¹² reported that the decrease in free length confirms the decreases in intermolecular distance, and the flexible structures are more compressible than rigid structures. Since bulk modulus plays an important role on the molecular structure, the relation between adiabatic bulk modulus and sound velocity is also important. The relation between the adiabatic bulk modulus and sound velocity of all tested oils is shown in the Table. While comparing with sound velocity, PFPE lubricants indicate higher density but lower adiabatic bulk modulus and Glycerol shows a large variation of density and adiabatic bulk modulus.

Usually, sound velocity decreases with the increase of density, but sound velocity increases with an increase of bulk modulus also. It is found that the value of bulk modulus impacts on the sound velocity in the lubricating oil. Here, density of PFPE oil is comparatively higher, but bulk modulus is lower. Sound velocity in the PFPE oil showed lower value. On the other hand, density of glycerol is lower than the PFPE oil but higher than that of the mineral oil, PAO oil and traction oil. Moreover, the bulk modulus of glycerol is greater than that of the other tested oils and belongs to higher sound velocity compared to others.

Surface tension is another important property of liquid lubricant, which is related to the molecular structure. It is the difference of the molecular attraction between one fluid and that with another at the interface that results in what we measure as surface tension. A liquid with low surface tension would spread easily on the solid surface and provide good lubrication. The relation between surface tension and the sound velocity is shown in the Table. The surface tension for the finished lubricants is sensitive to additives¹³.

It has been found that sound velocity decreases with the rise of temperature as shown in Figs. 1 and 2. The decrease in U with temperature indicated weakening of intermolecular forces due to thermal agitation. Usually

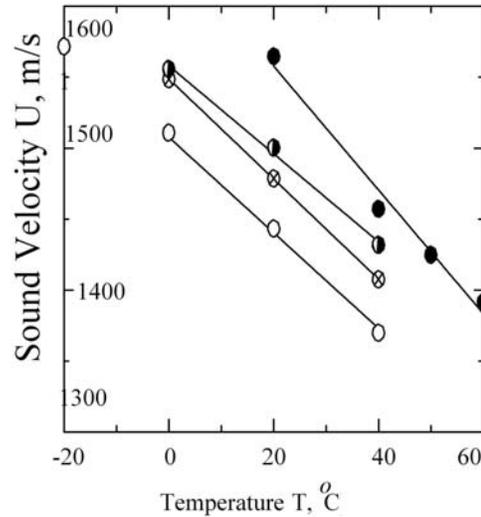


Fig. 1. Changes of sound velocity of paraffinic mineral oils P60N(\circ), P150N(\otimes), P500N(\bullet), PBSN(\bullet) with temperature.

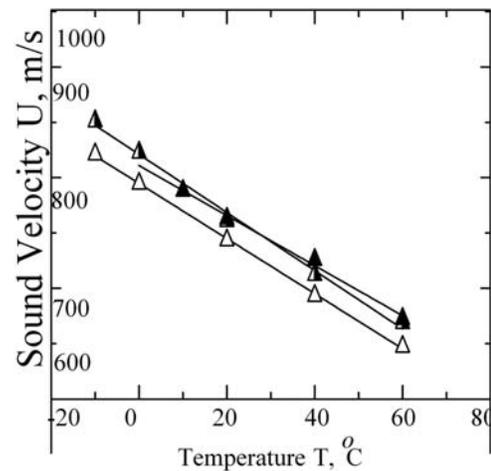


Fig. 2. Changes of sound velocity of per fluoropolyether oils Fomblin(Δ), Demnum (\blacktriangle), Krytox(\blacktriangle) with temperature.

sound velocity decreases with the increase of density but due to increase of the adiabatic bulk modulus, sound velocity increases. Sound velocity is an important property of lubricant. Sound velocity decreases with the increase of temperature and increases with the increase of bulk modulus. So, sound velocity of lubricating oils can indicates roughly the molecular structure of that lubricating oil as evident in the Table.

Conclusions

In the present work, we reported the theoretical results of sound velocity and bulk modulus for different

lubricating oils at different temperatures by utilizing the measured density, surface tension and sound velocity from the work of Mia and Ohno and it was found that theoretical results for sound velocity agrees well with the experimental finding when compared with experimental data. On that basis, it can be possible to find out the group which the lubricating oil behave. Mainly it is easy to classify the hydrocarbon oil (traction oil, PAO and paraffinic mineral oil), perfluoropolyether oil and glycerol. Behavior of traction oil, PAO and paraffinic mineral oils are almost similar since the hydrocarbon oil's molecular structure is almost similar. So it could be possible to identify unknown oil roughly.

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Ultrasonic absorption of uracil in aqueous solution

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The present paper reports the ultrasonic absorption and thermo-acoustic analysis of uracil in aqueous solution by ultrasonic non-destructive technique at different molar concentrations and temperatures. The non-linear and complex behaviour of uracil in aqueous medium helps to detect phase separation and strength of intermolecular interactions between the constituents in the aqueous solution of uracil.

Keywords: Uracil; thermo-acoustic parameters; ultrasonic absorption; Nomoto's relation.

Introduction

Ultrasonic absorption of uracil in aqueous solution by non-destructive technique is essential for utilizing them in biomedical technology. In biological sciences, nitrogenous bases are increasingly termed nucleobases because of their role in nucleic acids, their flat shape is particularly important when considering their roles as the building blocks of DNA and RNA. Ultrasonic wave velocity in a medium provides valuable information about the physical properties of the medium¹⁻³. It also provides important information about various inter and intra-molecular processes such as relaxation of the medium or the existence of isomeric states or the exchange of energy between various molecular degrees of freedom⁴⁻⁶. Ultrasonic parameters are extensively being used to study molecular interactions in pure liquids, binary liquid mixtures and ionic interactions in single and mixed salt solutions of bio-liquids⁷⁻⁸. The experimental investigations of ultrasonic absorption have shown that it provides a better insight into molecular processes.

Experimental

The liquids used were of BDH analar grade and were redistilled in the laboratory. In this study the measurements have been made in the temperature range 293 K-308 K. The temperature of the liquid mixture

was kept constant by the use of thermostat U-10 with ± 0.01 K accuracy. Density measurement was carried out by using hydrostatic sinker method with an accuracy $\pm 0.01\%$. A monopan electrical balance of least count as 0.0001 gm was used to record change in plunger weight dipped in the solutions correct to fourth place of decimal. Ultrasonic velocity measurements were made with an ultrasonic multi-frequency interferometer at frequency 4 MHz with an accuracy of $\pm 0.1\%$.

Results and Discussion

Figure 1 shows that the plot of experimental ultrasonic absorption (α/f^2) versus molar concentration at different temperatures 293K, 298K, 303K, 308K and 313K.

It is observed that the ultrasonic absorption (α/f^2) increases with increase in the molar concentration of uracil in distilled water.

It is also clearly seen that smaller the temperature, greater the ultrasonic absorption, indicating more stability of uracil molecules. Uracil molecule has four resonating structure which increases the relaxation time. Increase in relaxation time increases the ultrasonic absorption in this binary liquid system. The non-linear variation of ultrasonic absorption in each curve with molar concentration strongly supports the presence of intermolecular interactions through hydrogen bonding. The hydrogen bonding exists between oxygen atom of

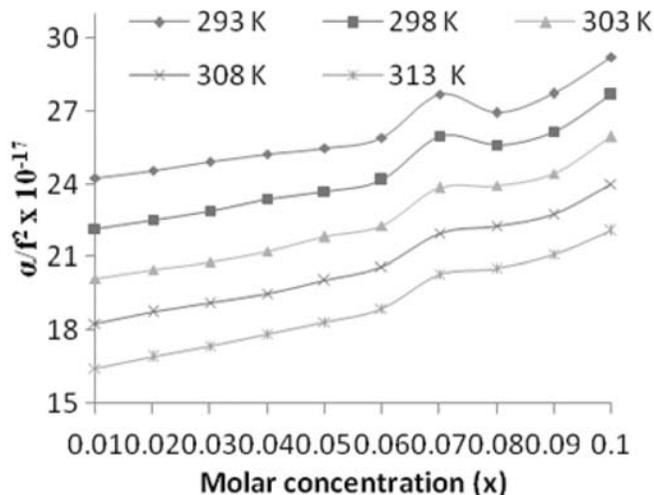


Fig. 1. Ultrasonic absorption with concentration. of aqueous solution uracil at different temperature.

uracil and hydroxyl group of water in the molecules of constituents this binary system.

The propagation of ultrasonic wave through binary liquid mixture disrupts thermal and structural equilibrium of the solution and produces energy transfer between different modes of the molecules. In this system structural relaxation plays a predominant role over thermal relaxation process. The decrease in ultrasonic absorption with increase in molar concentrations is due to the possible structural relaxation process in this binary system. From the Graph it is clear that, the remarkable peak is observed at molar concentration 0.07. This shows that, the constituent's molecules are more stable hence absorbs more ultrasonic energy.

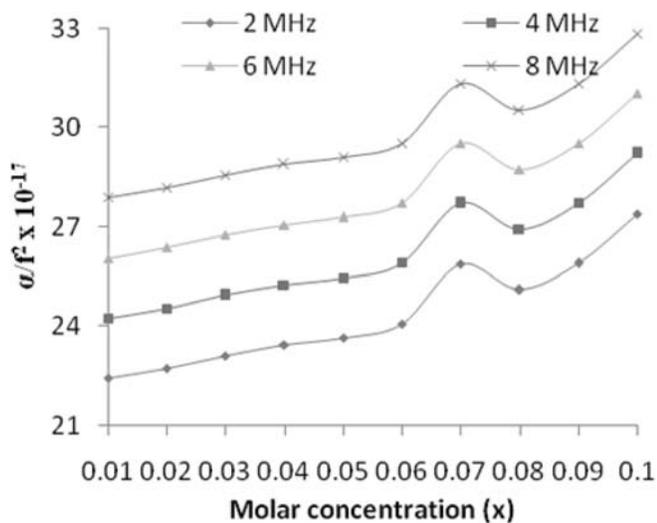


Fig. 2. Ultrasonic absorption vs conc. of aqueous solution of uracil at different frequency.

Figure 2 contains the plot of experimental ultrasonic absorption (α/f^2) versus molar concentration at different frequencies 2 MHz, 4 MHz, 6 MHz and 8 MHz.

It is observed that the ultrasonic absorption (α/f^2) increases with increase in the molar concentration of uracil in distilled water.

It is also clearly seen that smaller the frequency, less is the ultrasonic absorption. It is also observed that ultrasonic absorption (α/f^2) increases with increase in the molar concentration of uracil in distilled water, indicating more stability of uracil molecules. Uracil molecule has four resonating structure which increases the relaxation time. Increase in relaxation time increases the ultrasonic absorption in this binary liquid system. The non-linear variation of ultrasonic absorption in each curve with molar concentration strongly supports the presence of intermolecular interactions through hydrogen bonding. The hydrogen bonding exists between oxygen atom of uracil and hydroxyl group of water in the molecules of the constituents in this binary system. From the Graph it is clear that, the remarkable peak is observed at molar concentration 0.07. This shows that, the constituent's molecules are more stable hence absorbs more ultrasonic energy.

Figure 3 shows that the comparison of experimental ultrasonic velocities with molar concentration with theoretical values by different method.

Figure 3 shows the comparison of experimental ultrasonic velocity with theoretical values computed by empirical impedance dependence relation (IDR) and Nomoto's relation. It is observed that experimental ultrasonic velocity in aqueous solution of uracil are in good agreement with the values produced by empirical

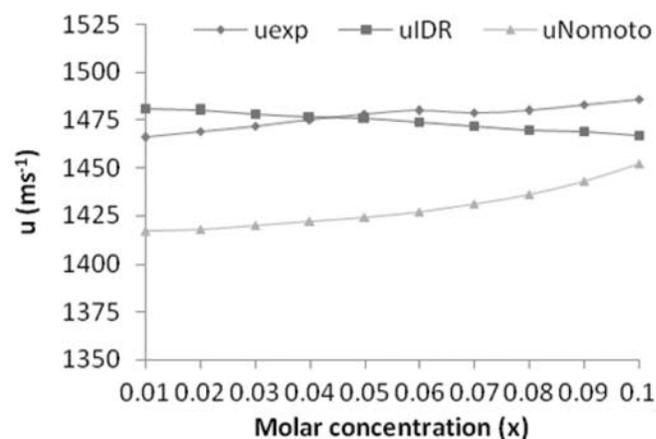


Fig. 3. Comparison of u vs molar conc. with theoretical values.

IDR and Nomoto's relation.

Conclusions

1. The non-linear variation of ultrasonic absorption in each curve with molar concentration strongly supports the presence of intermolecular interactions through hydrogen bonding.
2. Structural relaxation plays a predominant role over thermal relaxation. Increase in ultrasonic absorption with molar concentration is due to possible structural relaxation process.
3. The hydrogen bonding exists between oxygen atom of uracil and hydroxyl group of water in the molecules of the constituents in this binary system.

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Ph.D. Thesis Summary

Ultrasonic investigation of some nitrogenous bases in aqueous and acidic solution

(Awarded in 2017 by R. T. M. Nagpur University, Nagpur to Dr. P.D. Bageshwar, Department of Physics, Mungsaji Maharaj Mahavidyalaya, Darwha, Yavatmal, Maharashtra)

In recent years, nitrogenous bases have been attracted large attention of researchers all over the world. Ultrasonic studies are being carried out on a variety of liquids resembling nitrogenous bases. Nitrogenous bases have extensive use in the pharmaceutical industries. Therefore it was thought worthwhile to undertake the investigation on nitrogenous bases. Thesis presents Ultrasonic investigation of nitrogenous bases such as uracil, thymine, adenine and guanine in aqueous and acidic solution.

In the present work nitrogenous bases are solute, water and hydrochloric acids are solvent. Uracil, thymine and guanine are hydrogen, oxygen, and nitrogen bearing molecule, while adenine is hydrogen and nitrogen bearing molecule. All these nitrogenous bases are non-polar and both solvents are polar. Therefore the interaction and comparison of ultrasonic parameters of above aqueous and acidic liquids mixture was thought worthwhile.

For the study, binary liquid mixture were prepared in the laboratory which then taken in a doubled walled jacket liquid cell through which thermostat water circulated to produce a constant temperature using U-10.

The observed ultrasonic velocity, density, viscosity and derive parameters such as adiabatic compressibility, Isothermal compressibility, acoustic impedance, intermolecular free length, relative association, Vander Waal's constant, internal pressure, Rao constant, Wada constant, molar volume, free volume, inter-molecular radius, viscosity, relaxation time and absorption coefficient data for binary liquid mixtures has been reported.

The thesis is divided into six chapters. In the first chapter, the nature of ultrasound, propagation, detection of ultrasonic waves and applications of ultrasound in

various fields are briefly outlined. Peculiarities of liquid state, ultrasonic wave propagation in liquids, molecular interaction techniques, advantages of ultrasonic non-destructive technique, etc are also described in this chapter.

Broad review of the earlier work done by various workers in this field and orientation of present work are explained in the second chapter.

Third chapter deals with materials and methods used. Details about uracil, thymine, adenine and guanine were discussed. This chapter explains details of experimental technique such as ultrasonic interferometer, pulse echo overlap technique and other techniques. The procedural details of measurements of ultrasonic velocity and absorption employing interferometer method, density measurement using hydrostatic plunger method and viscosity measurement using Ostwald's viscometer in the temperature range 293 K to 313 K were discussed. The thermostat U-10 maintained the temperature of sample constant to the accuracy of ± 0.01 K.

Fourth chapter gives details of related theory and computational approach. It is observed that the strong intermolecular interactions exist in the systems of aqueous solution of all nitrogenous bases where as weak interaction is found to be in all acidic solution of nitrogenous bases. The association in the constituent molecules may involve due to hydrogen bonding or due to dipole-induced dipole interactions.

The results of all eight systems under investigation were explained in details and presented in fifth chapter and discussed. The comparative study has been discussed at the end of this chapter.

Sixth chapter deals with the summary and conclusions of the work.

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Given to Dr Periyannan Suresh for his thesis entitled "Ultrasonic Guided Waves for Measuring the Material Elastic Moduli and Temperature" from IIT, Madras under the guidance of Prof. Krishnan Balasubramaniam. At present he is Asstt. Professor at NIT Warangal.

ii. **Dr S. Parthasarthy Memorial Award for the year 2017**

Given jointly to two papers these are :

1. Computation of erosion potential of cavitation bubbles in ultrasonic pressure field by B K Sreedhar, S K Albert and A B Pandit, *J. Pure Appl. Ultrason.* **39**(2) (2017), 60-69.
From FRT Group, IGCAR, Kalpakkam 603102 and Instt of Chem Technology, Mumbai-400019
2. Study of Frequency and concentration dependence of Ultrasonic attenuation of NiO nanoparticle embedded in polyvinilidyne flouride by Chayan K. Karmakar, Biplab Dutta and Sampad Mukherjee, *J. Pure Appl. Ultrason.* **39**(2) (2017), 49-54.
From Deptt. of Physics, Indian Institute of Engineering Sci. and Technology, Shibpur, Hawarah-711103.

iii. **Dr. M. Pancholy Memorial Award** for Best ORAL presentation at WESPAC-2018 as annual event of the USI given to two papers out of more than 140 research papers presented in different stream of Ultrasonic and allied fields.

1. **Sensitivity and Acoustic Emission Performance of PVDF Sensor Sandwiched GFRP Composite Structure** By Jain Anjana and Minajagi Shivkumar WESPAC-2018, 11-15 Nov. CSIR-NPL, Delhi (2018) p 178.
From Material Sci. Division, National Aerospace Laboratory, Bangalore-560 017
2. **Acoustic Emission Investigation for Phase Transition between snow, ice and water** by Sharma Sakshi, Kapil J C, Shahi J S and Arora Roma WESPAC-2018, 11-15 Nov. CSIR-NPL, Delhi (2018) p 21.
From Snow Avalanche Study Establishment (SASE-RDC) DRDO Chandigarh-160036

iv. **Best Poster** presentation award at WESPAC-2018 as annual event of the USI given to two papers out of more than 100 research papers presented in the different stream of Ultrasonic and allied fields.

1. **Development of electro-acoustic stealth material for environmental noise reduction** by Mishra Sakti Prasad and Ganeswar Nath, WESPAC-2018, 11-15 Nov. CSIR-NPL, Delhi (2018)p 119.
From Veer Surender Sai University of Technology, Burla, Sambalpur, Orissa-768018
2. **Acoustical investigation of Ag/Pt bimetallic nanofluids** by Yadav Navneet, Yadav R R and Verma Alok Kumar, WESPAC-2018, 11-15 Nov. CSIR-NPL, Delhi (2018) p 133.
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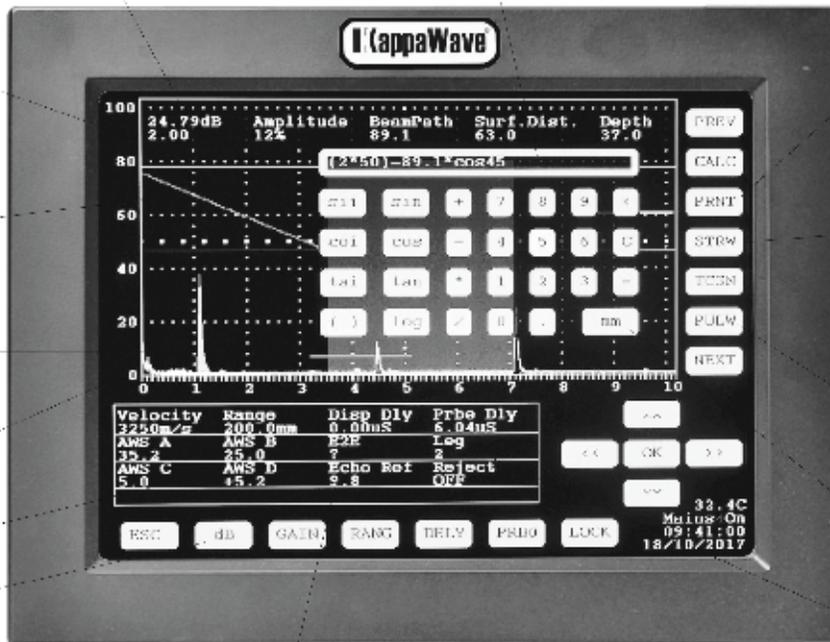
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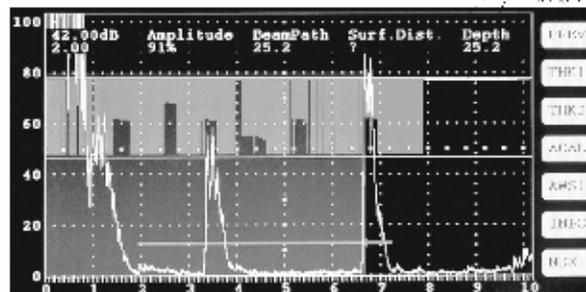
Leg info in an Angle beam test

- 26.4 & 17.7cm Touchscreen display
- Ease of use, All touch controls
- A, B Scan & Beam plot ability
- RF Wave
- 16GB memory
- 16 hours Li-ion battery
- PC Connectivity & Reporting software
- 14 point DAC & TCG
- AWS D1.1 Weld evaluation
- Echo Store for comparisons
- Scientific calculator
- Two point Auto calibration
- VGA out
- Adjustable PRF, Damping, Pulse width and Pulse energy
- New Reject control
- Low noise
- Penetrative power
- Clear visibility in any light

Model K1 with 26.4cm touchscreen display

Single Gate provides Echo to Echo distance

Material cross section in a R Scan



Two Point Auto Calibration

AWS D1.1 Weld evaluation

Easy to access functions

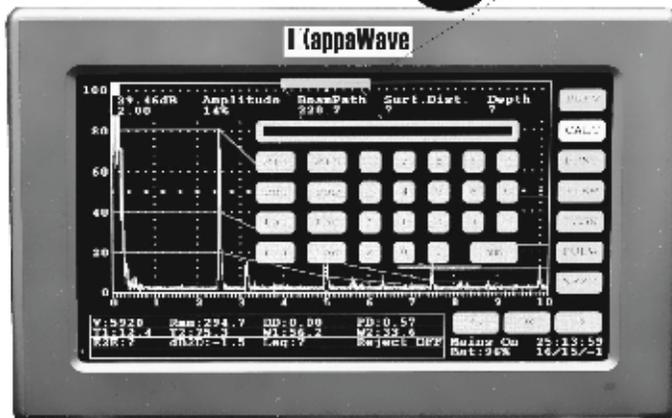
100 small divisions. 25mm to 6m Range in Steel

Select any file to open in computer

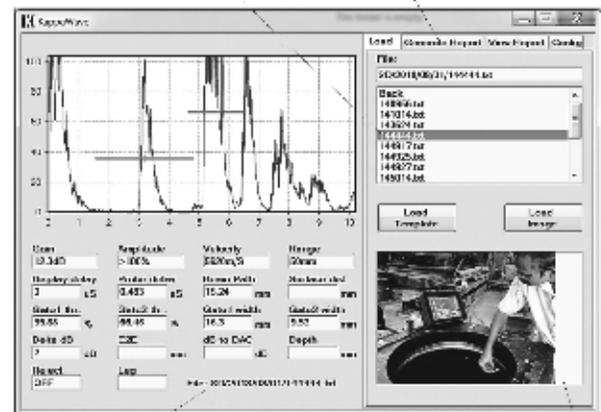
Enter data for report

1.2Kg
16Hr Li-Ion

Visual & Audible Alarm



Model K8 with 17.7cm touchscreen display



Test file info

Add photos or drawings to report

KAPPAWAVE