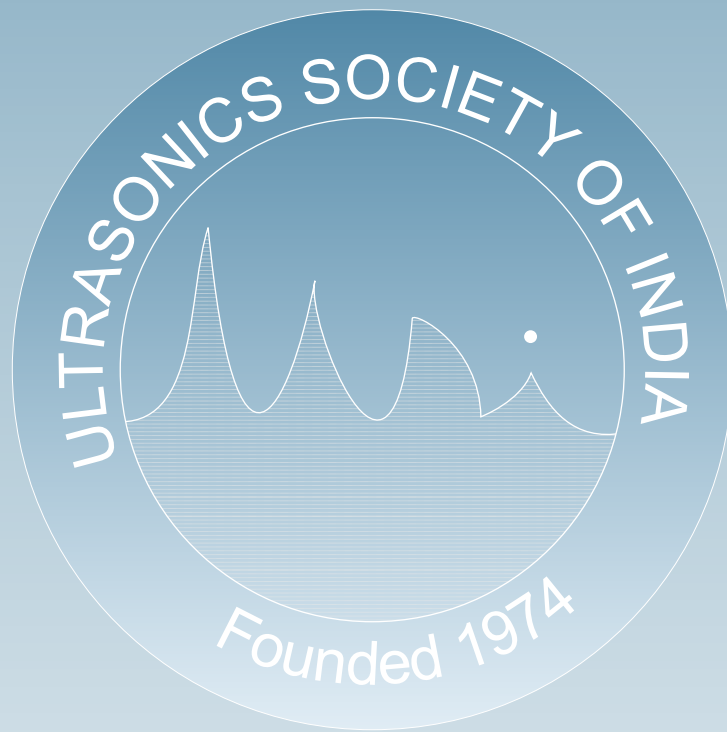


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Damage evaluation in high temperature stainless steel components using non-destructive techniques

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AISI type 310 stainless steel is currently in demand for the biomass gasifier plants in India as the main structural material. During operation of the plant this steel undergoes temperature as high as 1373K and variation in temperature and stress. In this work, we have received virgin and service exposed sample cut near the weld failure region of AISI type 304 SS suitably prepared and used for ultrasonic velocity measurements, acoustic emission testing (AET) and photoacoustic (PA) measurements on the virgin and service exposed specimens of AISI type 310 high temperatures steel with the aim to use the outcome of the study to increase the life cycle of the steel and hence the biomass plant. Acoustic emission (AE) test results indicate that as compared to the virgin specimens, strength increases and ductility decreases for the service-exposed specimens. AE generated is also higher for the service-exposed specimens as compared to the virgin specimens. Ultrasonic velocity measurements show comparatively higher velocity in service exposed specimen than in virgin specimen and the hardness measurements show opposite trend to that of ultrasonic measurements. The studies clearly indicate the immense possibility of the applying NDT techniques in assessing the service degradation taking place during the gasifier. In addition, Metallography and Photoacoustics (PA) measurements were also conducted on the specimens. It is found that PA measurements results found to correlate well with the above measurement results.

Keywords: Biomass gasifier, High temperature steel, Ultrasonic nondestructive testing

Introduction

Finding suitable and low cost alloys, which can operate at high temperatures, and simultaneously withstand cyclic temperature changes is a challenging job in boiler and biomass gas industries. A common factor of disadvantage is that materials in such environments may also undergo embrittlement at high temperatures. Even at low temperatures say below 1073K, the alloy is destined to fail due to reduction in toughness and ductility while subjecting it to cyclic variation in temperatures (from room temperature condition to the higher temperatures). At present AISI type 310 stainless steel is currently in demand for the biomass gasifier plants in India as the main structural material mainly due to its easy availability and cost.

A biomass gasifier system in its traditional version of development had been fabricated using high quality AISI type 310 stainless steel (high temperature stainless steel), for its reactor section. A schematic diagram of the gasifier is given in Fig. 1. Solid

biomass fed from the top of the system is pyrolysed in the middle zone of the reactor after the biomass passes through a drying zone. The pyrolysed gas

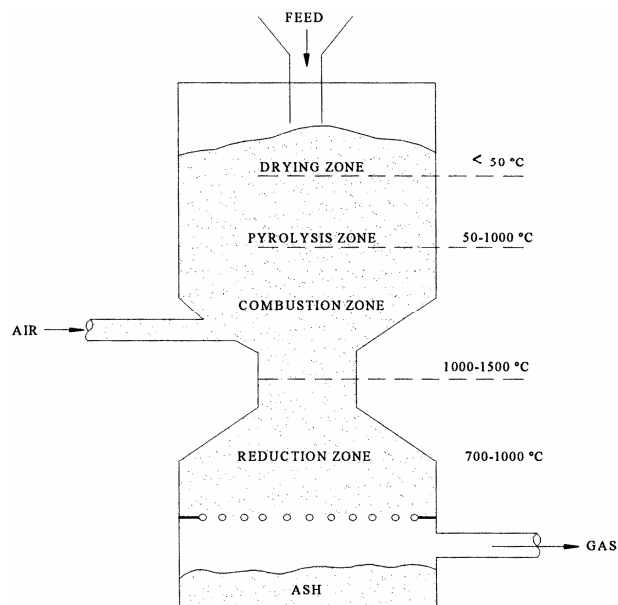


Fig. 1—Schematic diagram of a down draft gasifier

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mixture undergoes further reduction reactions and the final gas agglomerates are taken from the bottom of the gasifier systems

In order to ascertain that the gas coming out from the bottom strata of the system has undergone the reduction reaction fairly compliably, a 'throat' or restricted region is adopted in the design. In the earlier version of such reactors the throat region was exposed to high temperatures with fluctuations in the temperature profile. Due to intermittent operations, after shut off and start on sequences of the systems, the reactor around this region was experiencing cyclic thermal the reactor stress and hence after about 800 hours of operation the throat portion gave way by developing cracks.

A field study⁵ indicates that all gasifier technologies available in India are based on induced downdraft gasification and designed primarily for woody biomass. The major reason for the failure in most cases of the gasifier part is because of the failure of the structural material used for gasifier construction. Materials failure can be because of imperfect design, selection of improper material, intrinsic material flaws, and poor maintenance and service. The austenitic steel has been used for the construction of the gasifier. Material failures occur mainly in the gasifier throat and air nozzle regions and mostly within 1500 hours of operation. This is mainly because of the material of construction experiencing severe high temperature oxidation and corrosion during operation⁶. Added to this, design-specific problems also lead to greatly reduced life of the gasifier. Start-up and shutdown of the gasifier impose severe thermal strain on the material of construction. Depending on the operating conditions, in a typical gasifier, temperatures ranging from 1000 to 1300°C are reached in the hearth region within 10 minutes from the start of the operation. Hence, during operation the two major materials problems encountered in stainless steel-based gasifiers are corrosion and high temperature mechanical failure. Of the different grades of austenitic steel available, even the high-temperature grade, i.e., SS 310 is found to fail in the harsh environment encountered in the gasifier. It is susceptible to distortion due to low thermal diffusivity, severe oxidation, and intergranular separation at the surface and pitting.

Few examples of material related problems in gasifiers were reported earlier⁷.

1. Mark II gasifier of 3.7 KW rating having a hearth diameter of 90mm from M/s MMFE, India had undergone deformation at the lower portion of the cone after 200 hours of operation (Fig.2a).

2. In Ankur gasifier of 20KW having a hearth diameter of 85mm, there was a material failure at the throat after 500-800 hours of operation (Fig 2b).

Thus the macroscopic reason for the failure is broadly known leading to improvement of throat portion with ceramic lining in subsequent versions of gasifier systems. But no serious attempt was put to understand the microscopic details of the occurrence of such failures. The use of ultrasonic technique for microstructural characterisation in materials¹ and acoustic emission technique for characterizing the deformation behaviour^{2, 3} are well known. Here an attempt is made to understand this problem using acoustic emission studies on specimens taken from undamaged and damaged portion near the failure region of the throat. Ultrasonic studies were also carried out on the specimens with and without micro cracks. These studies would be helpful to understand the causes of failures and to prevent the occurrence of such failures in future and extend the service life of the gasifier. Additionally, PA measurements were also conducted to know the thermal properties of the specimens at different stages of the furnace operation.



Fig. 2—(a) Damaged part at the lower portion of Mark II gasifier.



Fig. 2— (b) Damaged throat portion of Ankur gasifier.

Specimen preparation

Part of the scrap from the failed throat region of a gasifier (put into operation of about 800 hours) was obtained and square specimens of 10mm x 10mm were cut. Specimens were cut far and near to the failed region. Approximate thickness of the scrap specimens were in this range was 1.5 to 1.7 mm. Similar size specimen was also prepared from virgin AISI type 310 stainless steel for comparison studies. The above specimens were useful for carrying out ultrasonic and hardness measurements, photoacoustic studies and metallographic examinations.

For AE studies, specimens were specially prepared for tensile testing purpose. Flat tensile specimens with gauge length of 12.5 mm and width 10 mm were prepared from the as-received and service damaged plates. These specimens were polished with 400grit emery paper to obtain uniform surface finish.

Metallographic examination

Metallographic examination was carried out to reveal the microstructure at different locations.

From the metallography (Fig. 3) the following observations were made:

- (i) There is continuous micro structural reformation taking place due to high temperature service exposure of the steel.
- (ii) The failure is due to the high temperature.
- (iii) The cracks are nucleated at different locations (multiple types)
- (iv) Cracks are nucleated from voids formed at the grain boundary junctions namely triple points
- (v) Cracks were propagated along the grain boundaries namely intergranular type of propagation.

The thermal fatigue effect is mainly attributed to the inherent weakness of the grain boundaries, which lead themselves to the formation of the induced grain voids that can enlarge into intergranular cavities and cracks. This change may be due to partial sensitization. The key-alloying element for this is carbon. Sensitization is a process by which the intergranular precipitation of chromium carbides in the region adjacent to grain boundaries occurs. This results in depletion of chromium. It depends on heating/cooling rates, heat treatment temperature and time. This occurs in the temperature of 723K to 1073K. This was investigated and verified through the X-ray measurement reported earlier⁴.

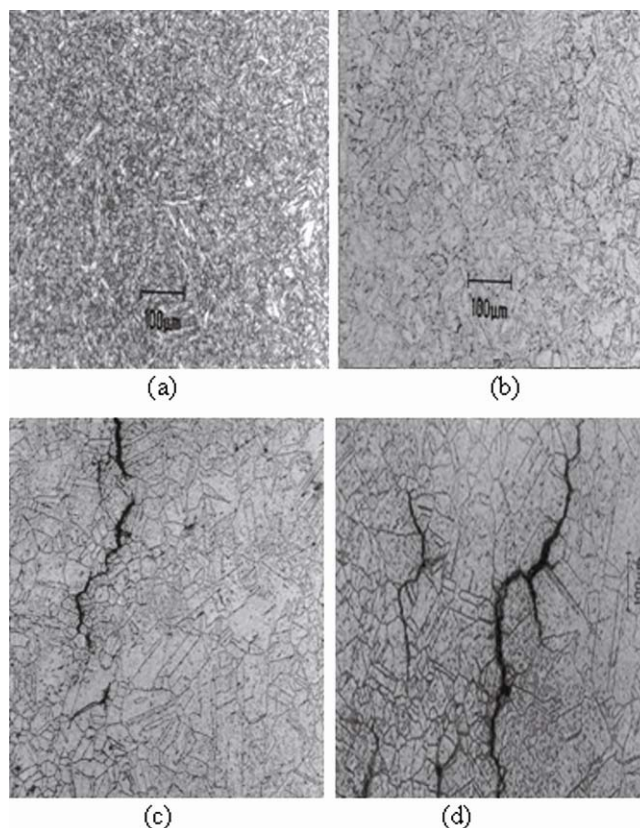


Fig. 3—Photomicrograph of the specimens (a) Virgin, (b) service exposed, (c) with multiple cracks and (d) service exposed with intergranular crack initiation.

Another problem with high-Cr, stainless steels is an embrittlement that occurs after longer times at elevated temperatures. This is attributed to the formation of “sigma phase” a brittle compound that forms at elevated temperature and goes the grain boundaries, thereby producing a brittle crack path through the metal. Stainless steels used in high temperature service should be checked periodically to detect sigma-phase formation¹¹.

Acoustic emission testing

The specimens were held in the grip of the tensile machine using pin-loaded arrangement. Tensile tests were carried out at nominal strain of $3.3 \times 10^{-4} \text{sec}^{-1}$ and at ambient temperature (300K) using tensile testing machine. Acoustic emission signals generated during the tensile tests were recorded and analyzed using an acoustic emission system. A piezoelectric transducer (15 mm dia.) having a resonant frequency at 150 kHz, a preamplifier with 60 dB gain and a compatible filter (100-300 kHz) were used to capture the AE signals. A total gain of 70 dB and a threshold of 40 dB were maintained throughout the experimental study. The worthiness of the AE data obtained using the specimen-sensor mounting assembly was verified by repeatedly loading and unloading a dummy specimen to more than 1.5 times the maximum load expected to be taken by any of the specimens used in the present study. The gain and the threshold were so selected that no external noise was recorded during the experiment. After the first cycle of loading, no emission was generated during the subsequent cycles. This ensured that the AE signal was not recorded either from the machine or from external noise.

The variations in nominal stress and AE count against nominal strain for the specimens in the as received and two service-damaged conditions are shown in Figs. 4a-4c. The variation in cumulative counts as a function of nominal strain for the above three types of specimens was computed upto uniform strain and is depicted in Fig 4.

It can be observed from Figs. 4a-4c that as compared to the as-received specimen (Fig.4a), strength (yield strength and ultimate tensile strength) increases and elongation (uniform elongation and total elongation) decreases for the service damaged specimens (Figs. 4b-4c). These results indicate that the two service-damaged specimens were in the cold worked condition as compared to the as-received specimen. Among all the specimens, specimen taken from the cracked plate (Fig. 4c) had experienced maximum amount of cold work as compared to the as received and other service-damaged specimen.

The results of acoustic emission depicted in Figs. 4a-4c and Fig.5 indicate that for all the specimens, AE is generated during yielding. For the specimen taken from the cracked plate (Fig. 4c), higher AE was observed immediately upon beginning of loading and strain levels upto around 7%. The variation of cumulative count as a function of strain is shown in Fig.5. This variation indicates that yielding is characterized by a change in slope at lower strain

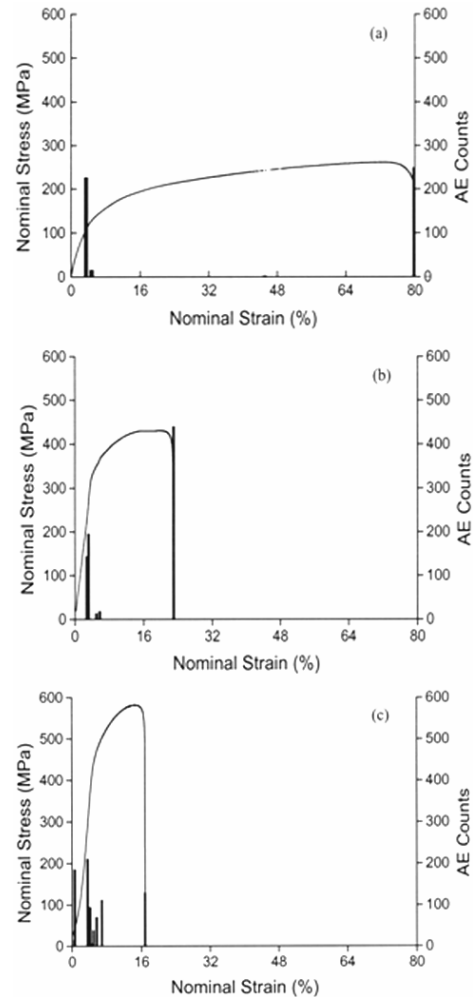


Fig. 4—AE counts during nominal applied stress.

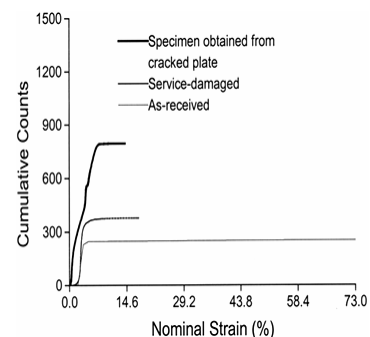


Fig. 5—Cumulative counts versus nominal strain for the three types of specimens.

levels for all the specimens. With increasing strain cumulative counts remain almost unchanged for the as-received specimen but for the other two service-damaged specimens increase in cumulative counts is observed and the increase in maximum for the specimen taken from the cracked plate.

During tensile deformation of metallic materials, the generation and motion of dislocations are the main activity-giving rise to AE signals. Intense AE is generated at low strain levels upto yielding. With progress in deformation, yielding is manifested by a peak of AE^{2,3}. Beyond yielding, generation of AE due to dislocation activity is reduced and this can be understood by the decrease in glide distance for moving dislocations and the reduced rate of formation of dislocation avalanche^{2,3}. The observed higher AE immediately upon beginning of loading and upto 7% strain for the specimen fabricated from the cracked plate (Fig. 4c), thus, indicates the presence of defects/flaws in this specimen. Generation of higher AE during deformation of specimens with defects/flaws has been reported earlier by Dunegan *et al.*⁸ and Palmer and Heald⁹. AE generated during necking elongation of all the specimens is negligible. The process of gradual necking down and subsequent fracture of the remaining ligaments (crack extension by microvoid coalescence) in stainless steel is known to be a quiet process².

In addition to the AE counts and cumulative counts, variations in other AE parameters during tensile deformation was analysed to understand the results. The data on amplitude, duration and rise time of the AE events was collected and analysed for the complete tensile testing and values of these parameters are shown in Table 1.

It could be seen from Table 1 that there is no appreciable variation in the values of event duration and rise time for the three types of specimens. Whereas the signals generated by the specimen obtained from the cracked plate had events with higher peak amplitude (upto 87 dB) as compared to the events generated by the as-received and other service-damaged specimens (upto 60 dB). This supports the results of AE counts that the presence of defects in the specimen taken from the cracked plate had generated events of higher peak amplitude.

Micro hardness and ultrasonic measurements

The Micro hardness measurements of as-received and service damaged samples were carried out using an indentation load of 50 gf with the help of a Leitz miniload-2 micro hardness measuring equipment as shown in Table 2.

Micro hardness value of the as-received specimens is found to be 290±5 VHN where as the micro hardness for the service damaged with micro cracks was found to be 254±5 VHN. This can be attributed to the fact that due to formation of microcracks in the service exposed material stress relaxation occurs and these results in reduced in hardness.

Correspondingly, ultrasonic velocity is found to be 5885 m/sec in the as received specimen and 6109 m/sec in the service damaged specimen. This difference in the velocity and hardness is attributed to the difference in their material properties to which the velocity and hardness are related. The variation is due to the microstructural changes. It includes the enlargement of grain voids by carbide precipitates at high temperature which is observed in the metallography. In case of the alloy [800H] investigated and it was shown that carbide precipitates formed as the temperature was increased and which hardened the structure¹⁰.

Photoacoustics measurements

Photoacoustics (PA) was first reported by A.G.Bell for the thin disk of samples using interrupted sunlight¹². Absorption of the photon excites a molecule into a higher vibrational state. Collision transfers the vibrational energy to translational energy in the form of heat. Modulation of light intensity (turning the light on and off) causes the temperature of the sample in a closed volume and this temperature variation is accompanied by a pressure variation which creates a sound wave that can be detected with a sensitive microphone.

PA Spectrometer

The Photo-acoustic setup was integrated with 500W Xenon light source, monochrometer, optical

Table 1—Comparison of amplitude, event duration and event rise time of AE events generated during tensile testing for the three specimens

Type of specimen	Range in the values of AE Parameters		
	Amplitude (dB)	Event duration (µm)	Rise time (µm)
As-received	42-60	0-1000	0-240
Service-exposed	42-58	0-1200	0-300
Specimen taken from cracked region (Service damaged)	42-87	0-1000	0-300

Table 2—Hardness and ultrasonic velocity for as received and service damaged specimens

Specimen	Hardness (VHN)	Longitudinal velocity (m/sec)	
		20 MHz	5MHz
As received	290±5	5885 ± 3	5908± 5
Service damaged	254±5	6109 ± 5	6081± 6

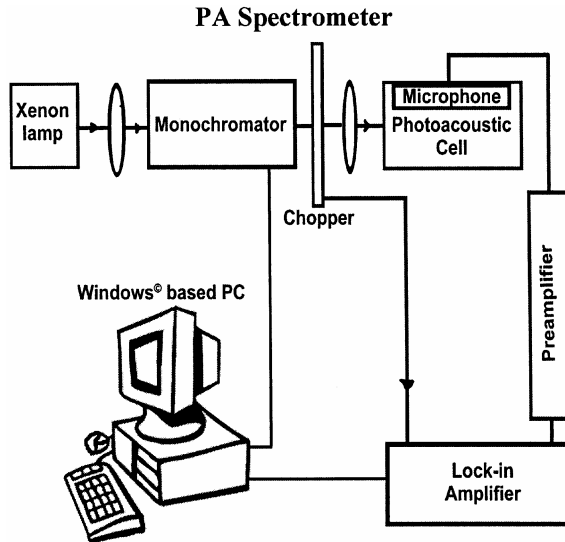


Fig. 6—Schematic diagram of the Photoacoustic spectrometer.

chopper, PA cell and microphone, lock-in-amplifier, Windows based PC. The instrument was automated and data acquisition was made in the computer. The whole system was installed and the instrument parameters were standardized with carbon block as the reference material (Fig. 6).

PA measurements

PA depth profile:

This is by keeping wavelength fixed, the chopping frequency is varied and the corresponding PA signals are observed. For thermal properties, depth profile is enough. Then the PA spectrum is given in the Figs.7(a)-7(c). The thermal diffusivity, thermal conductivity is calculated from these measurements using the standard relations. According to the Rosenwaig-Gersho theory the expression for the PA signal from one dimensional heat flux model for an optically opaque and thick sample can be obtained¹³.

Thermal diffusivity increases in the worn out sample compared to the as received and service exposed sample because the scattering in the alloy increases due to the defect and crack present in the sample. Thermal conduction is the size dependent phenomenon when the system size is comparable to the mean free path of the phonons in the system^{14,15}. Thermal conductivity is directly proportional to the thermal diffusivity. Thermal conductivity $K = \alpha \rho c_p$, where α is the Thermal diffusivity, ρ is the density and c_p is the specific heat capacity of the sample at constant pressure. The acoustic waves are basically, and these phonons will be very sensitive to the structural changes. Presence of grain boundary mismatches, defects, cracks etc. are expected to alter

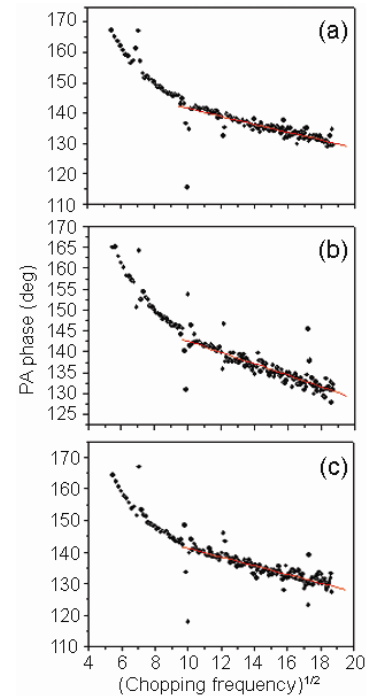


Fig. 7—PA spectra for depth profile analysis.

Table 3—Thermal diffusivity and thermal conductivity of AISI 310 stainless steel

Sample	Thickness mm	Thermal diffusivity ($\times 10^{-5} \text{ m}^2/\text{sec}$)	Thermal conductivity ($\text{m}^{-1}\text{K}^{-1}$)
As received	1.8	0.41	15.89
Service exposed Air Nozzle	2.3	0.89	34.49
Worn out Hearth	1.5	6.42	248.77

mean free path of phonons and this will be pronounced in the thermal conductivity. Hence it is expected that service exposed samples will have enhanced thermal conductivities. This is very much evident from Table 3 i.e. 2 times increase in case of service exposed specimen and more than 15 times in case of worn out specimen. The thermal diffusivity of the as received sample in our measurement is in good agreement with the value reported earlier¹⁶. The PA-measurements are important non-destructive evaluation tool to study particularly thermo mechanical properties.

Summary and conclusion

AISI type 310 stainless steel is a structural material for biomass gasifier system. Application of nondestructive test methods such as ultrasonics, acoustic emission, metallography, hardness measurements along with photoacoustic measurements have been demonstrated for the first time in AISI type 310 stainless steel. It is possible to characterize the different microstructure and deformation process in

AISI 310 stainless steel using acoustic methods. AE results are useful for monitoring the state of the materials under different deformation process at any given time. The ultrasonic and hardness measurements could be used for assessing the service damages prior to failure. The thermal parameters obtained from PA measurement also found to be very useful to characterize the material. This appreciable change in the thermal diffusivity is also reflected in the ultrasonic velocity. It is evident from the results the PA measurement and ultrasonic are important nondestructive tools to identify the microscopic variation in the degradation of internal condition of the structural material of the gasifier plant. Hence application of the above NDT methods along with photoacoustic technique would help the users to understand the physical mechanisms behind the premature failures of the components. This would help to extend the service life of the biomass gasifier plants which was mostly used as a rural technology for agriculture and power production.

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Ultrasonic investigation as a tool for assessing behaviour of multicomponent systems

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Ultrasonics has been a powerful tool for studying structural and physico-chemical properties of liquids, liquid mixtures and electrolytic solutions. Ultrasonic speed measurements are helpful for interpreting solute-solute, solute-solvent interactions in aqueous and co-aqueous medium in terms of derived parameters viz. Apparent molal Compressibility, Acoustic Impedance, Intermolecular Free Length etc. Bio-molecules play a vital role in the various biochemical processes occurring in living organisms. Their interactions studies throw a light on the structural complexity of these bio-molecules, which cannot be assessed directly. The present study provides new information from chemical and biological point of view to understand the interactions of threonine and dl-alanine in aqueous or co-aqueous DMF and uracil in the presence of Na₂SO₄ in aqueous urea solution.

Key words: Density, internal pressure, apparent molal volume, hydration number, ultrasonic velocity

Introduction

Experimental ultrasonic propagation parameters measurements in systems of electrolytes, non-electrolytes, biomolecules¹, carbohydrates, polymers, in aqueous and non-aqueous media are required for the extension of theoretical development by understanding the intermolecular forces in solutions and the structure-property relationships.

L-threonine is an essential amino acid that is important for the formation of collagen, elastin, and tooth enamel, and aids liver and lipotropic function when combined with aspartic acid and methionine². Threonine is an important constituent in many body proteins and is necessary for the formation of tooth enamel protein, collagen and elastin. Alanine plays a key role in glucose-alanine cycle between tissues and liver and also used in dosimetric measurements in radiotherapy. Maltose is an easy to digest carbohydrate, and is used in infant formulas, and in making beer³. Nucleic acids are one of the most important biomolecules present in biological system, and play an important role in the synthesis of genetic material. Uracil is nucleobase and essential part of RNA in genetic material and many viruses. DMF is used as a solvent to recover olefins such as 1,3-butadiene via extractive distillation and also used in the manufacturing of solvent dyes as an important raw material. Urea is commercially and industrially used to produce some types of plastics, animal feed, glues, detergents, pesticides and fungicides⁴. Aqueous urea

and its derivatives are important solvents and causes denaturation in protein and nucleic acid⁵.

Experimental

Threonine, dl-alanine, Urea and uracil were obtained from Himedia Chemicals Ltd. DMF from (Merck) and they were of Anala-R grade with >99 percent purity. Doubly distilled water was used for preparing solution. All the solutions were made on molality basis (m). For density measurement, pre calibrated bicapillary pycnometer is used with accuracy of $\pm 0.06\%$. Sound speeds have been measured using single frequency ultrasonic interferometer⁶ at 2 MHz having an accuracy of $\pm 0.04\%$. All the experimental data have been taken on thermostatically controlled water bath with circulating medium having an accuracy of $\pm 0.1^\circ\text{C}$. The weighing were done on electronic balance with accuracy of 0.1 mg.

Theory

The derived parameters have been calculated from experimentally measured values of density (ρ) and sound speed (u) of threonine in aqueous maltose and dl-alanine in water- DMF(1:1) and uracil in the presence of Na₂SO₄ in aqueous urea solution at 298,308 and 318 K using the earlier published theoretical relations⁸.

Results and Discussion

Sound speed in threonine+aqueous maltose, uracil+[aqueous urea (2M/3M/5M)+Na₂SO₄] and dl-alanine+

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Table-1: Density, sound speed, adiabatic compressibility, apparent molal volume of dl-alanine in water- DMF (1:1,v/v) at 298, 308 and 318 K.

C (mol.kg ⁻¹)	ρ (kg.m ⁻³)	u (m s ⁻¹)	β (10 ⁻¹⁰ m ² N ⁻¹)	Φ_v (10 ⁻³ m ³ / mol)
298K				
0	998.1	1689.6	3.5096	-
0.021	999.2	1694.4	3.4859	0.0366
0.042	1000.5	1700.0	3.4585	0.0318
0.063	1001.9	1706.4	3.4278	0.0286
0.0839	1003.4	1712.0	3.4003	0.0257
0.1049	1005.0	1717.6	3.3728	0.0231
308K				
0	980.2	1657.2	3.7148	-
0.021	980.6	1660.2	3.6999	0.0710
0.042	981.5	1663.4	3.6823	0.0586
0.063	982.3	1666.6	3.6652	0.0561
0.0839	983.2	1670.4	3.6452	0.0535
0.1049	984.3	1674.8	3.6220	0.0500
318K				
0	973.1	1624	3.8965	-
0.021	973.5	1626.4	3.8834	0.0714
0.042	974.2	1630	3.8635	0.0638
0.063	975.1	1634.0	3.8410	0.0579
0.0839	976.2	1638.0	3.8180	0.0524
0.1049	977.2	1642.4	3.7937	0.0501

Table-2: Apparent molal compressibility, acoustic impedance, intermolecular free length, free volume, internal pressure and hydration number of dl-alanine in water- DMF (1:1, v/v) at 298, 308 and 318 K.

C (mol.kg ⁻¹)	$-\phi_k$ (10 ⁻¹¹ m ² N ⁻¹)	Z (10 ⁶ kg m ⁻² s ⁻¹)	L _f (A°)	V _f (10 ⁻⁸ m ³ mol ⁻¹)	π_i (10 ⁹ Nm ⁻²)	n _H
298K						
0	-	1.6864	0.3852	1.0441	2.3558	-
0.021	1.3143	1.6930	0.3839	1.0364	2.3614	11.1390
0.042	1.4182	1.7009	0.3824	1.0293	2.3670	12.0155
0.063	1.5086	1.7096	0.3807	1.0235	2.3719	12.8189
0.0839	1.5186	1.7178	0.3792	1.0163	2.3780	12.8432
0.1049	1.5271	1.7262	0.3776	1.0091	2.3843	12.8611
308K						
0	-	1.6244	0.4035	1.6325	2.0727	-
0.021	0.7985	1.6280	0.4027	1.6013	2.0850	6.6269
0.042	0.9088	1.6326	0.4018	1.5703	2.0982	7.2216
0.063	0.9310	1.6371	0.4008	1.5407	2.1110	7.3477
0.0839	0.9812	1.6423	0.3997	1.5128	2.1236	7.7308
0.1049	1.0488	1.6485	0.3985	1.4872	2.1356	8.2434
318K						
0	-	1.5803	0.4207	2.2847	1.9039	-
0.021	0.7187	1.5833	0.4200	2.2564	1.9108	5.5408
0.042	0.9145	1.5879	0.4189	2.2222	1.9200	6.9856
0.063	1.0332	1.5933	0.4177	2.1792	1.9322	7.8240
0.0839	1.1089	1.5990	0.4164	2.1449	1.9424	8.3070
0.1049	1.1624	1.6050	0.4151	2.1109	1.9525	8.7045

water-dimethyl formamide (DMF) show a general increase with concentration and temperature indicating breaking of hydrogen bonds as temperature rises. Density increases with concentration and decreases with temperature. The increase with concentration explains the solute-solvent interactions to be present in the system. The increase in concentration increases the electrolytic nature of solute towards solvent (Table-1, 4, 7). The apparent molal volume⁹ of threonine in aqueous maltose, dl-alanine in co-aqueous DMF and of uracil in [aqueous urea (2M/3M/5M)+Na₂SO₄] mixed solvent system as a function of molal concentration has been determined at 298, 308 and 318K. The plots of ϕ_v with \sqrt{C} have been fitted in Mason's equation

$$\phi_v = \phi_v^o + S_v \sqrt{C}$$

where ϕ_v^o is the limiting apparent molal volume and S_v is the experimental slope. Table1,4,7 show the positive values of ϕ_v^o in aqueous maltose, co-aqueous DMF and aqueous urea +Na₂SO₄ mixed solvent system, which indicates the presence of strong solute solvent interactions. The negative values of S_v^* imply weak solute-solute interactions.

The isentropic compressibility ϕ_k has proved to be very sensitive to changes in solvation, H-bond and water structural changes¹⁰ in aqueous and co-aqueous medium (Table-2,5,8). The limiting apparent molal compressibility ϕ_k^o is generally negative for all the systems studied, which show solute-solvent interactions. The magnitude of compressibility depends upon electrostriction and throws a light on hydrophobic-hydrophilic interactions in solution. The negative values indicate hydrophobic interactions and loss of structural compressibility due to increased population of H-bonded water molecules. The negative values of S_k^* indicates weak solute-solute interactions in dl-alanine+co-aqueous DMF and uracil+aqueous urea systems in the presence of Na₂SO₄ while in the threonine+ aqueous maltose

Table-3: Limiting apparent molal volume (ϕ_v^o), experimental slope (S_v^*), apparent molal compressibility (ϕ_k^o) and experimental slope (S_k^*) of dl-alanine in water- DMF (1:1,v/v) at 298,308 and 318 K.

	ϕ_v^o (10 ⁻³ m ³ mol ⁻¹)	S_v^* (10 ⁻³ m ³ lt ^{1/2} mol ^{-3/2})	ϕ_k^o (10 ⁻¹⁰ m ² N ⁻¹)	S_k^* (10 ⁻¹⁰ N ⁻¹ m ⁻¹ mol ⁻¹)
298K	0.0488	-0.0801	-1.0489	-1.6538
308K	0.0895	-0.1298	-0.5042	-1.7043
318K	0.0930	-0.1378	-0.3930	-2.4450

Table-4: Density and sound speed, adiabatic compressibility, apparent molal volume, of L-Threonine+aqueous Maltose(0.01M) at 298,308 and 318 K

C (mol.kg ⁻¹)	ρ (kg.m ⁻³)	u (m/s)	β (10 ⁻¹⁰ .m ² N ⁻¹)	Φ_v (10 ⁻³ m ³ mol ⁻¹)
298K				
0	990.2	1494.0	4.5245	---
0.1022	994.0	1509.8	4.4133	0.0823
0.2045	996.2	1515.6	4.3700	0.0901
0.3067	1001.1	1523.6	4.3029	0.0833
0.4089	1005.0	1533.6	4.2307	0.0824
0.5112	1009.3	1543.4	4.1595	0.0810
0.6134	1013.2	1553.8	4.0880	0.0805
308K				
0	988.1	1514.2	4.4139	---
0.1022	992.2	1528.0	4.3167	0.0795
0.2045	995.6	1534.2	4.2671	0.0825
0.3067	999.4	1541.0	4.2137	0.0823
0.4089	1003.4	1548.8	4.1547	0.0813
0.5112	1007.5	1555.8	4.1004	0.0803
0.6134	1011.7	1562.0	4.0512	0.0795
318K				
0	986.0	1528.0	4.3439	--
0.1022	990.1	1541.6	4.2501	0.0798
0.2045	993.5	1547.4	4.2037	0.0827
0.3067	997.2	1553.6	4.1545	0.0824
0.4089	1001.1	1559.6	4.1066	0.0817
0.5112	1005.3	1565.6	4.0584	0.0807
0.6134	1009.1	1571.6	4.0123	0.0805

system positive values indicate comparatively strong solute-solute interactions (Table-3, 6, 10).

The values of adiabatic compressibility (β) decreases with concentration in all the mixed solvent systems and increases with increase in temperature in dl-alanine co-aqueous DMF and uracil+aqueous urea+Na₂SO₄ mixed solvent system while decreases in the threonine+aqueous maltose system. The decrease in the adiabatic compressibility is due to the electrostrictive compression of water¹¹ around solute molecules (Table-1,4,9).

Table-2,4,8,9 show the values of apparent molal compressibility (ϕ_k), acoustic impedance (Z), intermolecular free length (L_f), free volume (V_f), internal pressure (π_i) and hydration number (n_H). Intermolecular free length (L_f), free volume (V_f) and hydration number (n_H) decrease with increases with increase in concentration of solute. The decrease in free length with increase of solute concentration suggest that there is significant interactions between solute and solvent molecules and increase with temperature is due to thermal expansion of the solvent¹². Lyophobic interactions increase the

intermolecular distance and becomes responsible for the propagation of sound waves. The formation of tight solvation layer around the solute zwitterions is responsible for the decrease in free volume and vice-versa increase in the internal pressure with the addition of solute at particular temperature. With increase of temperature the bonds weaken and hence the values of V_f increase. Positive hydration/solvation number indicates structure forming tendency¹³ of solute at all temperatures. The values indicate that closer approach of unlike molecules is due to hydrogen bonding¹⁴. The positive values of molal hydration number (n_H) indicate the presence of dipole-

Table-6: Limiting apparent molal volume (ϕ_v^*), experimental slope (S_v^*), apparent molal compressibility (ϕ_k) and experimental slope (S_k^*) of L-Threonine +aqueous Maltose (0.01M) at 298,308 and 318 K

	S_v^* ($10^{-3} \text{ m}^3 \text{ l}^{1/2}$ $\text{mol}^{-3/2}$)	ϕ_v^* ($10^{-3} \text{ m}^3 \text{ mol}^{-1}$)	$S_k^*/$ (10^{-10} N^{-1} $\text{m}^{-1} \text{ mol}^{-1}$)	ϕ_k^* ($10^{-10} \text{ m}^2 \text{ N}^{-1}$)
298K	-0.0029	0.0834	0.9357	-1.2990
308K	0.0036	0.0793	1.0195	-1.2491
318K	0.0045	0.0792	1.0381	-1.2088

Table-5: Apparent molal compressibility, acoustic impedance, intermolecular free length, free volume, internal pressure and hydration number of L-Threonine + aqueous Maltose(0.01M) at 298, 308 and 318 K

C (mol.kg ⁻¹)	$-\phi_k$ ($10^{-10} \text{ m}^2 \text{ N}^{-1}$)	Z (10^6 kg $\text{m}^{-2} \text{ s}^{-1}$)	L_f (A°)	V_f ($10^{-7} \text{ m}^3 \text{ mol}^{-1}$)	π_i (10^{12})N m^{-2}	n_H (10^{-3})
298K						
0	--	1.4794	0.4373	15.2650	5.0307	---
0.1022	1.2557	1.5008	0.4319	3.0545	5.1304	2.4575
0.2045	0.8862	1.5099	0.4298	2.9667	5.1714	1.7077
0.3067	0.8775	1.5254	0.4265	2.7765	5.2382	1.6327
0.4089	0.8725	1.5413	0.4229	2.6638	5.3102	1.6237
0.5112	0.8693	1.5577	0.4193	2.5865	5.3839	1.6134
0.6134	0.8646	1.5743	0.4157	2.4758	5.4597	1.6080
308K						
0	--	1.4962	0.4399	21.5650	5.3527	--
0.1022	1.1297	1.5161	0.4350	4.3088	5.4485	2.2024
0.2045	0.8791	1.5275	0.4325	4.1847	5.5007	1.6628
0.3067	0.8108	1.5400	0.4298	3.9327	5.5581	1.5118
0.4089	0.7915	1.5540	0.4267	3.7494	5.6228	1.4679
0.5112	0.7710	1.5675	0.4239	3.6392	5.6844	1.4204
0.6134	0.7484	1.5803	0.4214	3.4967	5.7421	1.3697
318K						
0	--	1.5066	0.4442	28.8530	5.6500	--
0.1022	1.0957	1.5263	0.4393	5.8007	5.7492	2.1602
0.2045	0.8462	1.5373	0.4369	5.5980	5.8018	1.6139
0.3067	0.7750	1.5493	0.4344	5.3575	5.8587	1.4531
0.4089	0.7368	1.5614	0.4319	5.1217	5.9157	1.3659
0.5112	0.7152	1.5739	0.4293	4.9386	5.9744	1.3145
0.6134	0.6945	1.5859	0.4269	4.7171	6.0316	1.2724

Table-7: Density and sound speed of uracil in [aqueous urea (2M/3M/5M)+Na₂SO₄ (2M)] at 298,308 and 318 K

C(mol kg ⁻¹)	ρ (kg m ⁻³)			u (m s ⁻¹)		
	2M			2M		
	298K	308K	318K	298K	308K	318K
0	1129.5	1125.1	1121.4	1695.6	1678.8	1648.8
0.0079	1130.1	1125.6	1121.8	1703.2	1686.4	1664.2
0.0158	1130.8	1126.2	1122.3	1704.4	1687.2	1665.4
0.0237	1131.5	1126.8	1122.8	1705.6	1688.6	1666.2
0.0316	1132.2	1127.4	1123.3	1706.6	1689.8	1667.4
	3M			3M		
	298K	308K	318K	298K	308K	318K
0	1133.1	1126.1	1123.4	1709.6	1688	1667.6
0.0079	1133.8	1126.7	1123.9	1713.2	1691.8	1671.2
0.0157	1134.6	1127.4	1124.5	1714.4	1692.2	1671.6
0.0236	1135.4	1128.1	1125.1	1715.2	1692.8	1672.4
0.0315	1136.2	1128.9	1125.9	1715.6	1693.2	1672.8
	5M			5M		
	298K	308K	318K	298K	308K	318K
0	1137.4	1131.7	1126.5	1726	1711.6	1702.8
0.0078	1138.2	1132.4	1127.1	1729.6	1715.2	1706.4
0.0157	1139.1	1133.2	1127.8	1730.4	1715.6	1706.8
0.0235	1140.0	1134.2	1128.5	1730.8	1716.2	1707.2
0.0314	1140.9	1134.6	1129.2	1731.2	1716.8	1708.2

Table-8: Apparent molal volume, apparent molal compressibility of uracil in [aqueous urea (2M/3M/5M)+Na₂SO₄ (2M)] at 298,308 and 318 K

C (mol kg ⁻¹)	(Φ_v) (10 ⁻³ m ³ /mol)			S_k^* (10 ⁻¹¹ m ² N ⁻¹)		
	2M			2M		
	298K	308K	318K	298K	308K	318K
0.0079	0.0397	0.0496	0.0597	1.1834	1.5213	1.8597
0.0158	0.0348	0.0446	0.0547	1.0425	1.3766	1.7231
0.0237	0.0332	0.0430	0.0530	0.9952	1.3261	1.6774
0.0316	0.0324	0.0422	0.0522	0.9717	1.3005	1.6525
	3M			3M		
	298K	308K	318K	298K	308K	318K
0.0079	0.0296	0.0394	0.0494	0.8777	1.2076	1.5603
0.0157	0.0246	0.0343	0.0443	0.7275	1.0535	1.4011
0.0236	0.0231	0.0328	0.0427	0.6852	1.0078	1.3519
0.0315	0.0224	0.0296	0.0370	0.6650	0.9083	1.1686
	5M			5M		
	298K	308K	318K	298K	308K	318K
0.0078	0.0197	0.0293	0.0392	0.5653	0.8673	1.1806
0.0157	0.0150	0.0245	0.0343	0.4295	0.7270	1.0359
0.0235	0.0132	0.0227	0.0292	0.3796	0.6744	0.8811
0.0314	0.0127	0.0147	0.0269	0.3634	0.4347	0.8101

Table-9: Adiabatic compressibility, acoustic impedance and free length of uracil in [aqueous urea (2M/3M/5M)+Na₂SO₄ (2M)] at 298,308 and 318 K

C (mol.kg ⁻¹)	β (10 ⁻¹⁰ m ² N ⁻¹)			Z (10 ⁶ Kg m ⁻² s ⁻¹)			L _f (Å°)		
	2M			2M			2M		
	298K	308K	318K	298K	308K	318K	298K	308K	318K
0	3.0794	3.1536	3.2802	1.9152	1.8888	1.8490	0.3608	0.3718	0.3860
0.0079	3.0504	3.1239	3.2186	1.9248	1.8982	1.8669	0.3591	0.3701	0.3824
0.0158	3.0442	3.1193	3.2126	1.9275	1.9001	1.8691	0.3588	0.3698	0.3820
0.0237	3.0380	3.1124	3.2081	1.9299	1.9027	1.8708	0.3584	0.3694	0.3817
0.0316	3.0326	3.1064	3.2020	1.9322	1.9051	1.8730	0.3581	0.3690	0.3814
	3M			3M			3M		
0	3.0196	3.1166	3.2010	1.9371	1.9009	1.8734	0.3573	0.3696	0.3813
0.0079	3.0050	3.1009	3.1858	1.9524	1.9062	1.8783	0.3564	0.3687	0.3804
0.0157	2.9987	3.0976	3.1826	1.9454	1.9078	1.8797	0.3561	0.3685	0.3802
0.0236	2.9938	3.0934	3.1778	1.9474	1.9096	1.8816	0.3558	0.3682	0.3799
0.0315	2.9903	3.0898	3.1740	1.9493	1.9115	1.8834	0.3556	0.3680	0.3797
	5M			5M			5M		
0.0000	2.9512	3.0162	3.0616	1.9632	1.9370	1.9182	0.3532	0.3636	0.3729
0.0078	2.9369	3.0017	3.0470	1.9686	1.9423	1.9233	0.3524	0.3627	0.3720
0.0157	2.9319	2.9982	3.0437	1.9711	1.9441	1.9249	0.3521	0.3625	0.3718
0.0235	2.9282	2.9935	3.0404	1.9731	1.9465	1.9266	0.3518	0.3622	0.3716
0.0314	2.9245	2.9903	3.0350	1.9751	1.9479	1.9289	0.3516	0.3621	0.3713

Table-10: Limiting apparent molal volume (ϕ_v^*), experimental slope (S_v^*), apparent molal compressibility (ϕ_k^*) and experimental slope (S_k^*) of uracil in [aqueous urea (2M/3M/5M)+Na₂SO₄ (2M)] at 298,308 and 318 K

Parameters	298K			308K			318K		
	2M	3M	5M	2M	3M	5M	2M	3M	5M
ϕ_v^* (10 ⁻³ m ³ mol ⁻¹)	0.0463	0.0360	0.0261	0.0563	0.0485	0.0435	0.0664	0.0612	0.0519
S_v^* (10 ⁻³ m ³ lt ^{1/2} mol ^{-3/2})	-0.0823	-0.0808	-0.0806	-0.0833	-0.1058	-0.1518	-0.842	-0.1304	-0.1434
ϕ_k^* /(10 ⁻¹¹ m ² N ⁻¹)	1.3735	1.0640	0.7437	1.7206	1.4829	1.2869	2.0459	1.9306	1.5641
S_k^* /(10 ⁻¹¹ N ⁻¹ m ⁻¹ mol ⁻¹)	-2.3814	-2.3857	-2.2989	-2.4853	-3.2182	-4.4898	-2.3265	-4.1103	-4.3147

dipole interactions between solute and solvent molecules. An increase in temperature decreases molal hydration number due to the weakening of solute-solvent interactions.

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Ultrasonic velocity and absorption studies on some amino acids in water-aprotic solvent mixtures

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Ultrasonic velocity and absorption studies have been carried out in the amino acids namely glycine and β -alanine in Water-dioxane, Water-tetrahydrofuran and Water-dimethylformamide mixed solvents. These studies are carried out in the amino acid concentration range of 0.1 to 0.8 molar at a fixed frequency of 5 MHz and at a fixed temperature of 303K. The ultrasonic velocity in aqueous solutions of amino acids containing 10% V/V of dioxane, tetrahydrofuran and dimethylformamide increases non-linearly with increase of concentration of amino acids. The non-linear increase in ultrasonic velocity is explained on the basis of ionic hydration, hydrogen bonding and the structure breaking power of various aprotic solvents used. The observed absorption has been explained as due to ionic hydration, weakening of hydrogen bonds and proton transfer reactions occurring in these solutions.

Keywords: Ultrasonic velocity, ionic hydration, proton transfer, ultrasonic absorption.

Introduction

Amino acids belong to an important family of biomolecules which serve primarily as the basic building blocks of all proteins. Proteins play many different biological roles in the living systems. Proteins are the molecular instruments through which all genetic informations are expressed¹. Several works on partial molal adiabatic compressibility, ultrasonic, volumetric and viscometric studies²⁻⁹ of some amino acids in aqueous solutions of electrolytes, sugars and alcohols have been reported in the literature in order to understand their behavior in aqueous environment. From a survey of literature, the study of molecular interactions of amino acids in water-aprotic solvent mixtures is scanty. Hence, in order to shed more light on the nature of molecular interactions of amino acids in water-aprotic solvent mixtures, ultrasonic velocity and absorption studies are carried out in aqueous solutions of glycine and β -alanine containing 10% v/v of dioxane (DN), tetrahydrofuran (THF) and dimethylformamide (DMF) in the present work. It is more useful to extend the ultrasonic studies of amino acids to water-aprotic solvent mixtures because aqueous mixed solvents are extensively used in chemistry and other fields to control factors such as solubility, reactivity and stability of systems. In addition to this, the biological fluids are ultimately not pure water and hence this type of study would help us

to understand the physiological role of biological fluids in a much better way.

Materials and Method

The amino acids used in the present study are of AR/BDH grade and they are used as such without further purification. The solvents used namely dioxane, tetrahydrofuran and dimethylformamide are of spectroscopic grade. Triply distilled deionised water is used for preparing the solutions of amino acids. Ultrasonic velocity and absorption studies are carried out at a fixed frequency of 5 MHz in the concentration range 0.1 molar to 0.8 molar of glycine and β -alanine. Ultrasonic velocity studies are carried out using a multiple frequency ultrasonic interferometer. The ultrasonic absorption studies are made using Pulsed Power Oscillator. Both ultrasonic velocity and absorption studies are carried out at a fixed temperature of 303K by circulating water from a thermostatically controlled water bath and the temperature being maintained to an accuracy of $\pm 0.1^\circ\text{C}$. The accuracy of velocity measurement is ± 2 parts in 10^4 . Shear viscosity and density of aqueous solutions of glycine and β -alanine containing 10% v/v of dioxane, tetrahydrofuran and dimethylformamide are determined using an Ostwald's viscometer and a graduated dilatometer respectively. From the measured values of velocity, density, viscosity and observed absorption, various other parameters

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such as adiabatic compressibility, intermolecular free length and classical absorption are calculated using standard equations¹⁰.

Results and Discussion

The ultrasonic velocity and observed absorption measured in aqueous solutions of amino acids and in aqueous solutions of amino acids containing 10% v/v of dioxane, tetrahydrofuran and dimethylformamide increases non-linearly with increasing concentration of amino acids. The variation of ultrasonic velocity, adiabatic compressibility, intermolecular frelength and observed absorption with concentration of amino acids (glycine and β -alanine) studied are shown graphically in Figs.1-8.

Ultrasonic velocity studies in aqueous amino acids

When glycine is dissolved in water, the amino (NH_2) and carboxylic (COOH) groups present in glycine strongly interact and exist as dipolar ions namely NH_3^+ and COO^- . The water monomers already present in the medium surround these dipolar ions of glycine due to strong electrostatic attraction leading to the formation of ionic hydration. This strengthens the cohesion among the water molecules present in the medium. The increased cohesion in the medium brings about an increase in ultrasonic velocity and decrease of adiabatic compressibility in aqueous solutions of glycine as shown in Figs.1 and 2 respectively. On increasing the concentration of glycine, the ultrasonic velocity also increases. This may be due to the fact that the increase in concentration of glycine leads to increased ionic hydration^{11,12}. This in turn further strengthens the cohesion among the water molecules in the medium. This invariably leads to further increase of ultrasonic velocity. The variation of frelength with concentration (Fig.3) also supports this. The explanation offered for the velocity and compressibility studies in ultrasonic velocity and adiabatic compressibility for aqueous solutions of glycine also holds good for aqueous solutions of β -alanine (Figs 4, 5 and 6) in the concentration range studied.

Ultrasonic velocity studies in aqueous amino acids with 10% v/v of dioxane, tetrahydrofuran and dimethyl formamide

When 10% v/v of each dioxane, tetrahydrofuran and dimethylformamide is added to aqueous solutions of amino acids, a further increase in ultrasonic velocity is observed. This can be explained as follows using 'Flickering Cluster Model of Liquid Water'.

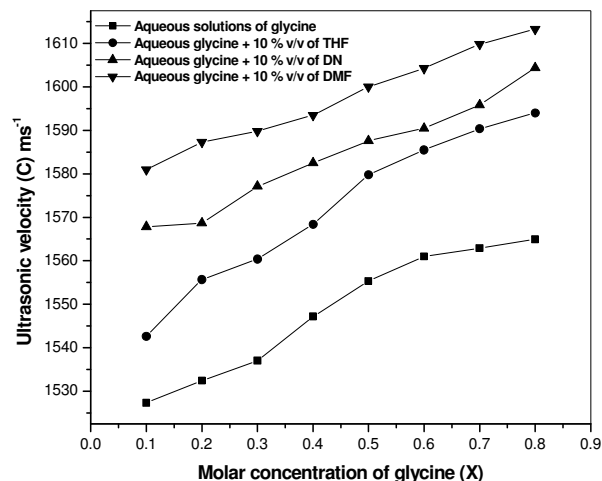


Fig. 1—Variation of ultrasonic velocity (C) with molar concentration (X) of glycine

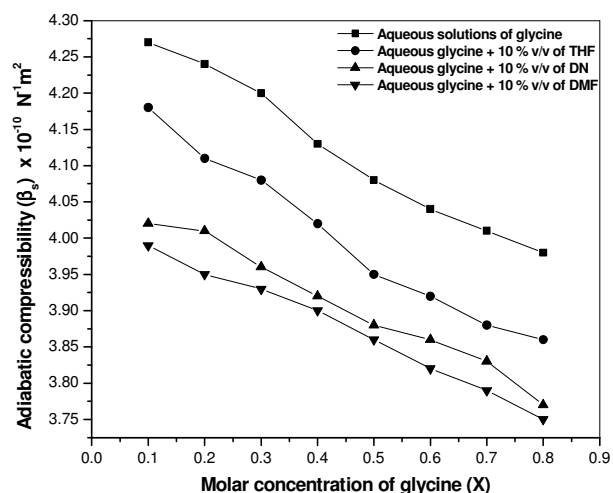


Fig. 2—Variation of adiabatic compressibility (β_s) with molar concentration (X) of glycine.

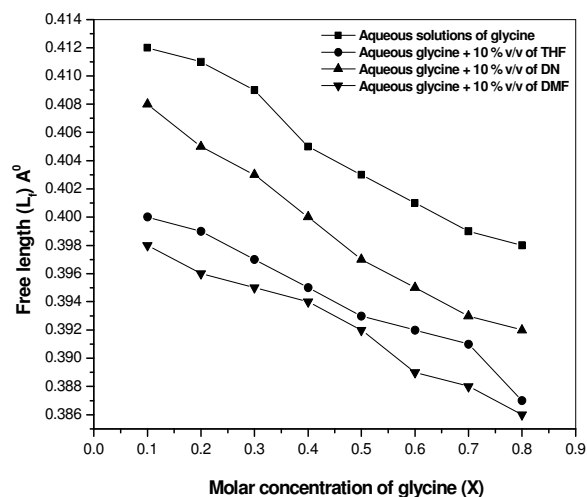


Fig. 3—Variation of free length (L_f) with molar concentration (X) of glycine.

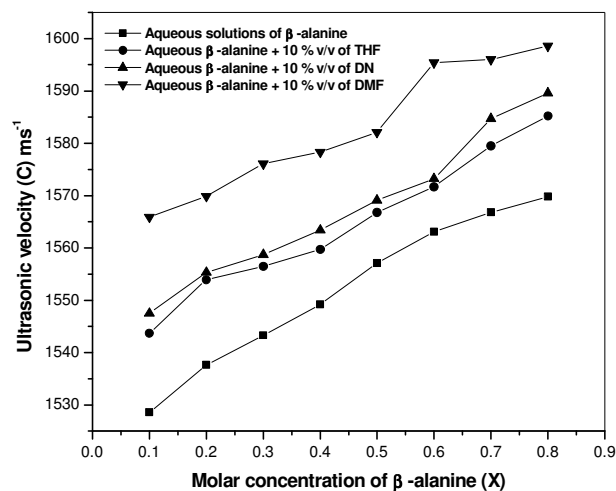


Fig. 4—Variation of ultrasonic velocity (C) with molar concentration (X) of β -alanine.

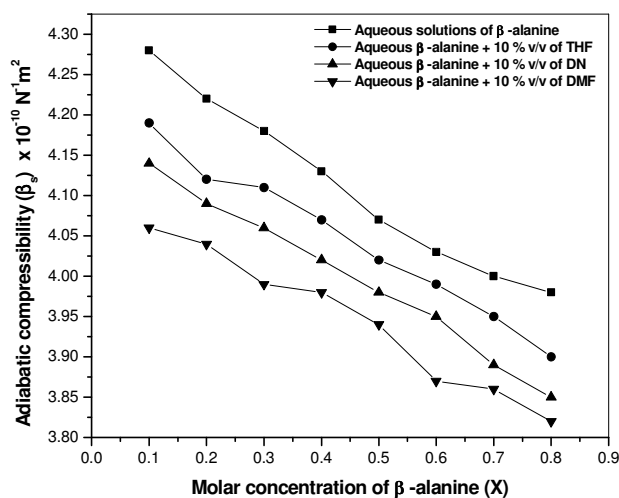


Fig. 5—Variation of adiabatic compressibility(β_s)with molar concentration (X) of β -alanine.

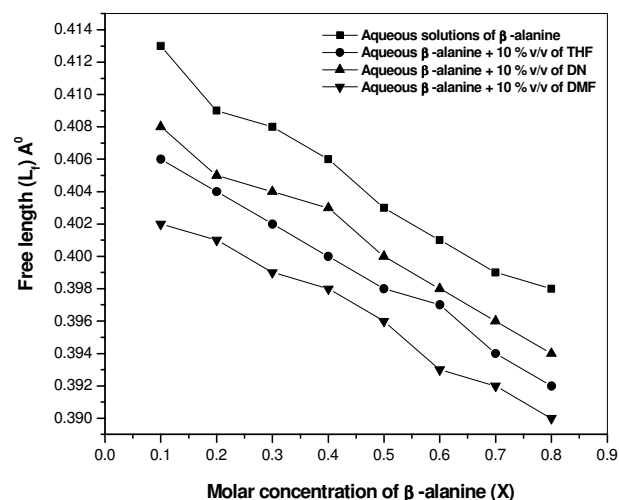


Fig. 6—Variation of frelength (L_f) with molar concentration (X) of β -alanine.

According to this model, water is supposed to consists of less dense hydrogen bonded clusters called ‘Open packed structure’ and high dense non-bonded water molecules called ‘Close packed structure’. Water is a dynamic mixture of these two. The breakdown of clusters is a co-operative process, when one hydrogen bond in the cluster breaks down the whole cluster breaks down and increases the population of high dense close packed structure of water i.e. dense monomers¹³.

When 10% v/v of dioxane is added to aqueous solutions of amino acids, dioxane breaks the hydrogen bonds in the open packed structure of water thereby releases high dense water monomers. The released water monomers may form hydrogen bonds with two free oxygen of dioxane molecule. Also, the released water monomers may surround the dipolar ions of the amino acids leading to the formation of ionic hydration sheath. Both these effects lead to strengthening of cohesion among the water molecules in the medium. This leads to a further decrease of adiabatic compressibility and increase of ultrasonic velocity in aqueous solutions of amino acids with 10% v/v of dioxane as shown in Figs 1, 2, 4 and 5. Thus, one can expect a higher value of ultrasonic velocity in aqueous solutions of amino acids containing 10% v/v of dioxane as compared to aqueous solutions of amino acids. A similar effect may also take place in aqueous solutions of amino acids containing 10% v/v of tetrahydrofuran and dimethylformamide respectively.

The ultrasonic velocity measured in aqueous solutions of amino acids with 10% v/v of dioxane is found to be slightly higher than the velocity measured in aqueous solutions of amino acids with 10% v/v of tetrahydrofuran in the entire amino acid concentration range studied. This may be due to the fact that each dioxane molecule has two free oxygens for the formation of hydrogen bonds with water molecules whereas each tetrahydrofuran molecule has only single free oxygen for hydrogen bonding. As a result, the cohesion in aqueous solutions of amino acids containing 10% v/v of dioxane must be slightly higher than the cohesion in aqueous solutions of amino acids with 10% v/v of tetrahydrofuran.

The ultrasonic velocity measured in aqueous amino acids with 10% v/v of dimethylformamide is found to be higher than the ultrasonic velocity measured in other two systems namely 10% v/v of tetrahydrofuran and 10% v/v of dioxane. This can be attributed to the higher values of donor number and dipole moment of dimethylformamide compared to dioxane and

tetrahydrofuran. In general, the difference in the ultrasonic velocity measured in aqueous solutions of amino acids containing 10% v/v of dioxane, tetrahydrofuran and dimethylformamide for any particular concentration of amino acid may be attributed to the difference in the structure breaking power, donor number and dipole moment of these aprotic solvents¹⁴⁻¹⁶.

Ultrasonic absorption studies

The observed ultrasonic absorption measured in aqueous solutions of amino acids and in aqueous amino acids containing 10% v/v aprotic solvents increases non-linearly with increasing concentration of amino acids as shown in Figs. 7 & 8. Moreover, the observed absorption is found to be several times

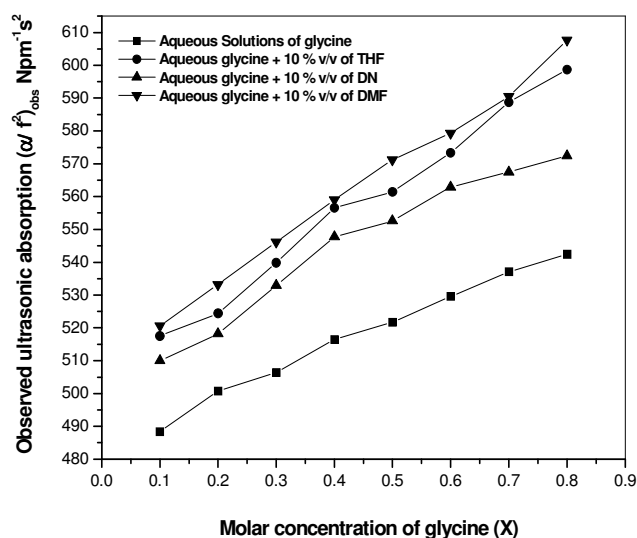


Fig. 7—Variation of observed ultrasonic absorption $(\alpha / f^2)_{\text{obs}}$ with molar concentration (X) of glycine.

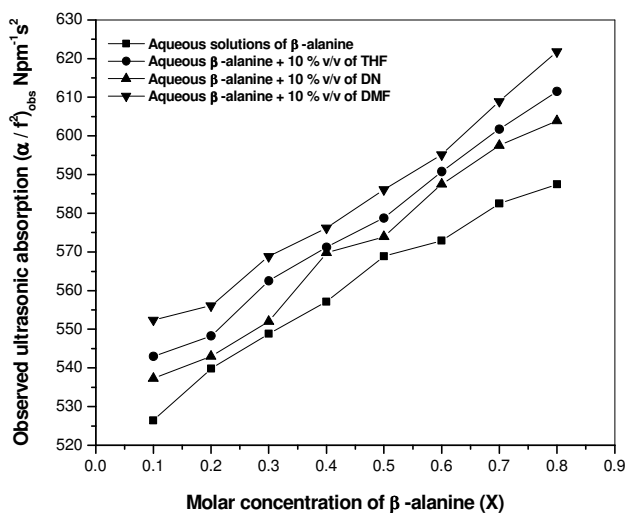


Fig. 8—Variation of observed ultrasonic absorption $(\alpha / f^2)_{\text{obs}}$ with molar concentration (X) of β-alanine.

(nearly 9 times) higher than the classical absorption ($5.7 - 6 \text{ Npm}^{-1}\text{s}^2$) indicating that the large value of observed absorption is not only due to shear viscosity alone, but some other mechanisms are also responsible for observed absorption in the present studies¹⁵. This can be explained as follows:

When an amino acid is dissolved in water, it dissociates and exists in dipolar form called 'zwitterions'. Water molecules are attached strongly to these zwitterions by electrostatic forces which introduce a greater cohesion among the water molecules leading to ionic hydration. The cohesion due to ionic hydration in these solutions generally increases with increase of amino acid concentration. This increased cohesion will bring about an increase in the ultrasonic absorption^{17,18} and such an increase in absorption is observed in the present study in aqueous solutions of amino acids (glycine and β-alanine).

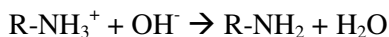
When 10% v/v of dioxane is added to aqueous solutions of glycine and β-alanine, the following effects takes place:

- i Dioxane breaks the open packed structure of water and thereby releases water monomers. The released water monomers form hydrogen bonds with the two oxygen of dioxane molecule. When ultrasonic waves pass through the medium, part of its energy is used in weakening or breaking of hydrogen bonds already formed. So, it is very likely that during the compression cycle of ultrasonic wave, hydrogen bonds are pushed closer resulting in a partially irreversible weakening or breaking of hydrogen bonds due to the absorption of ultrasonic energy. As the pressure wave has passed through the medium completely, hydrogen bonds are formed again between dioxane and water molecules. Such type of making and breaking of intermolecular bonds as the pressure wave passes on through the medium contributes to the observed increase in ultrasonic absorption.
- ii The released water monomers may surround the dipolar ions of amino acids leading to the formation of ionic hydration. This increases the cohesion among the water molecules, thus leading to increased ultrasonic absorption.

Both of these effects taking place in aqueous solutions of glycine and β-alanine with 10% v/v of dioxane contribute significantly to the observed ultrasonic absorption. The above explanation offered for aqueous solutions of amino acids containing 10% v/v of dioxane is also equally applicable for aqueous

solutions of amino acids containing 10% v/v of tetrahydrofuran and 10% v/v of dimethyl formamide.

According to Applegate *et al.*,¹⁹ perturbation of proton-transfer equilibrium



also contributes significantly for the observed ultrasonic absorption. This process also leads to increased cohesion between the water molecules and hence to an observed increase in ultrasonic absorption.

Conclusion

The ultrasonic velocity measured in aqueous solutions of glycine and β -alanine increases non-linearly with increasing concentration of these amino acids due to ionic hydration taking place in the solutions. When 10% v/v of each dioxane, tetrahydrofuran and dimethyl formamide is added to aqueous solutions of amino acids, the non-linear increase in ultrasonic velocity is both due to ionic hydration and the formation of hydrogen bonds in the mixed solutions. The observed ultrasonic absorption in both the amino acids studied increases with increase of amino acid concentration due to ionic hydration, making and breaking of hydrogen bonds and proton transfer reactions taking place in the solutions.

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Ultrasonic investigation on surfactants in the presence of builders and fillers

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Surfactants and builders are the two most important ingredients in laundry, household and personal-care cleaning products. They play a key role in washing processes. The enzyme Lipase is coupled with three fillers in the presence of aqueous surfactants builder solutions to study the efficiency of the detergent in the removal of dye colour through acoustical investigations. Ultrasonic velocities (U) and densities (ρ) are measured for different solutions at 303K using thermostatically controlled water bath whose temperature was maintained to an accuracy of $\pm 0.01^\circ\text{C}$. Acoustical Parameters such as adiabatic compressibility (β), free length (L_f), acoustic impedance (Z) and surface properties like surface tension (γ), surface area (Y) and molar surface energy (E) are determined.

Keywords: Surfactants, builders, fillers, enzyme-Lipase, acoustical parameters.

Introduction

In recent years, several research workers have investigated the molecular interactions in soaps, metallic soaps and detergents in the presence of added electrolytes^[1-4]. Surfactants are usually organic compounds which are amphiphilic and they are soluble in both organic solvents and water. Surfactants have two parts, one is hydrophilic (water loving) and another is hydrophobic (water repellent). By reducing the surface tension of water, surfactants improve the cleaning performance by enabling the solution to wet a surface quickly and effectively, and hence the soil can be readily loosened and removed. Surfactants also emulsify oily soils and keep them suspended and dispersed so they do not settle back on the surface. In order to make the detergents cheap and user friendly, inorganic and organic diluting agents are added as detergent builders. Detergent builders enhance the quality of the water, thereby make the detergents work in a more effective and efficient manner. Further detergent fillers as additives can be added in detergents to improve the cleansing performance.

Enzymes are biological catalysts and have been used for many years as isolating agents particularly in the food industries^[5]. Enzymes are proteins that are capable of removing stains caused by organic substances because of stronger interactions between enzymes and molecules responsible for stains.

Several researchers have given importance on enzymes as detergents^[6-7]. At present, Proteases and amylases are used as bio-detergents^[8]. Recently lipases are also found to be suitable in detergent preparation. Bio-detergents are effective even in

micro-amounts and they are biodegradable. They do not leave harmful residues. Bio-detergents have low negative impact on sewage-disposal processes and do not pose a threat to the aquatic life. In the present investigations, the enzyme lipase is coupled with fillers in the presence of aqueous surfactant builder solutions and the efficiency of the detergents in the removal of dye colour has been investigated by acoustical studies.

Experimental

Anionic surfactant Sodium Dodecyl Sulphate [SDS] is chosen ($\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$) as it is popular in the detergent industries. SDS has good detergent action because it has the wetting power and high emulsification efficiency. It is also used in the electrophoresis separation of proteins and lipids. This compound is also used as a foaming agent in tooth paste. Besides, the organic diluting agent Sodium Carbonate (Na_2CO_3) is chosen as builder which is basically a water softener that are used to soften wash water by extracting and binding the magnesium calcium ions in wash water. It also upgrades and the cleaning efficiency of surfactant. With this, different detergent fillers namely NaCl, Na_2SO_4 and ethanol as additives are added in detergents to improve the cleansing performance. These influence the detergent action of surfactants by changing the surface tension (γ) and molar surface energy (E). It is necessary to investigate the interaction between the surfactant and builder- filler molecules.

AnalaR grade samples of Sodium Dodecyl Sulphate (SDS), Sodium Carbonate, Sodium Sulphate, Sodium Chloride, Ethanol, Crystal Violet

dye (CV) and Lipase were used as such and distilled water was prepared by distillation technique. Accurately weighted amounts of the sample were dissolved in triple distilled water to obtain solution of different Concentrations. The ultrasonic velocities of the solutions were measured using an ultrasonic interferometer with a single crystal at a frequency of 2 MHz. The accuracy in the velocity measurement is $\pm 2\text{m/s}$. The densities of solutions were measured at 303K using specific gravity bottles with an accuracy of $\pm 0.001\text{kg/m}^3$. The cell temperature was maintained constant at 303K by an ultra-thermostat maintained at an accuracy of $\pm 0.01^\circ\text{C}$.

Theoretical Formulations

The acoustical parameters such as adiabatic compressibility (β), free length (L_f), surface tension (γ), molar surface energy (E) and surface area (Y) were calculated from the measured ultrasonic velocity (U) and density (ρ) of aqueous solutions of the surfactant in the presence of builder (Sodium Carbonate), different fillers (Sodium Sulphate, Sodium Chloride and Ethanol) and crystal violet dye with lipase at 303K. The following equations were used in these calculations

Adiabatic compressibility	$\beta = (1/U^2 \rho)$	$\text{kg}^{-1}\text{ms}^2$
Free length	$L_f = K (\beta)^{1/2}$	10^{-10}m
Surface tension	$\gamma = (U^{3/2} 6.3 \cdot 10^{-4}) \rho$	Nm^{-1}
Molar surface energy	$E = \gamma V_m^{2/3}$	Jmol^{-1}
Surface area	$Y = (36 \Pi N V_a)^{1/3}$	$\text{m}^2\text{mol}^{-1}$
Acoustic impedance	$Z = \rho U$	$\text{kgm}^{-2}\text{s}^{-1}$

Where U = Ultrasonic velocity (m/s), ρ = density (Kg/m^3), V_m = Molar Volume (m^3), V_a = Available Volume (m^3), K = Jacobson’s constant.

Results and Discussion

The ultrasonic velocity and density values are measured for aqueous solution of surfactant at 303K in the presence of added builder at different concentrations with different fillers. The molality of the surfactant is maintained at 10mM. The enzyme lipase is coupled with fillers in the presence of aqueous surfactant builder solutions and the efficiency of the detergents in the removal of dye colour has been investigated by acoustical studies.

Table 1 shows the acoustical parameters of aqueous solution of SDS with various concentrations of builder (Na_2CO_3) while Table 2 shows the acoustical parameters of aqueous solutions of SDS - builder with different fillers. It is observed from the Table that the ultrasonic velocity of the solutions increased by varying the concentrations of builder. Consequently the adiabatic compressibility of the solutions decreases as expected indicating the strong interaction of builder with the surfactant. The behaviour of intermolecular free length is similar to that of adiabatic compressibility in all the solutions studied. The variation of acoustic impedance supports the same. The increase in γ , E and Y indicates the enhancement of surfactant with different concentrations of builder. The addition of different fillers with the surfactant helps to improve the cleansing performance. Filler added in the detergent alters the physical characteristics which are well supported by FTIR analysis.

In order to establish the enhancement of detergent action by lipase, acoustical properties are calculated for crystal violet (CV) dye with detergent. In this study the dye concentration is kept constant (0.25mM). The detergent concentration is fixed at

Table 1—Acoustical Parameters of aqueous solution of SDS with various concentrations of builder

Concentration/ 10^3 gm/cc		(ρ) kgm^{-3}	(U) ms^{-1}	$\beta (10^{-10})$ kg^1ms^2	L_f 10^{-10}m	$\gamma (10^4)$ Nm^{-1}	E(10^2) Jmole^{-1}	Y(10^6) $\text{m}^2\text{mole}^{-1}$	Z(10^6) $\text{kgm}^{-2}\text{s}^{-1}$
SDS	Na_2CO_3								
0.0288	0.000	1001.692	1531	4.256	0.4123	3.7830	39.710	46.393	1.534
0.0288	0.010	1010.989	1539	4.174	0.4086	3.7847	47.698	48.286	1.556
0.0288	0.020	1020.278	1557	4.043	0.4021	3.9490	48.725	42.962	1.589
0.0288	0.030	1036.803	1578	3.873	0.3936	4.0945	50.083	34.209	1.636
0.0288	0.040	1047.137	1584	3.806	0.3902	4.1589	50.609	30.688	1.659
0.0288	0.050	1052.293	1597	3.723	0.3859	4.2337	51.382	16.048	1.681

Table 2—Acoustical Parameters of aqueous solutions of SDS - builder with different fillers [SDS] = 10 mM Temperature = 303 K

Solutions with fillers	(ρ) kgms^{-3}	(U) ms^{-1}	$\beta(10^{-10})$ kg^1ms^2	L_f 10^{-10}m	$\gamma (10^4)$ Nm^{-1}	E(10^2) Jmole^{-1}	Y(10^6) $\text{m}^2\text{mole}^{-1}$	Z (10^6) $\text{kgm}^{-2}\text{s}^{-1}$
NaCl	1015.121	1547	4.115	0.4057	3.8924	50.215	44.405	1.571
Na_2SO_4	1017.182	1550	4.092	0.4046	3.9105	55.200	46.998	1.577
Ethanol	1018.692	1554	4.063	0.4031	3.9328	48.854	42.461	1.583

Table 3—Acoustical Parameters of aqueous solutions of SDS-builder-filler-Crystal Violet (CV) dye- Lipase
[SDS] = 10 mM Temperature = 303 K

Solution	(ρ) kgms ⁻³	(U) ms ⁻¹	$\beta(10^{-10})$ kg ⁻¹ ms ²	L_f 10 ⁻¹⁰ m	$\gamma(10^4)$ Nm ⁻¹	E(10 ²) Jmole ⁻¹	Y(10 ⁶) m ² mole ⁻¹	Z(10 ⁶) kgm ⁻² s ¹
SDS - Na ₂ CO ₃ -NaCl - CV	1019.219	1540	4.1321	0.4066	3.8805	56.153	51.992	1.5696
SDS - Na ₂ CO ₃ -NaCl - CV-Lipase	1020.284	1550	4.0785	0.4039	3.9232	60.772	53.461	1.5815
SDS- Na ₂ CO ₃ - Na ₂ SO ₄ -CV	1021.317	1551	4.0677	0.4034	3.9820	62.568	50.795	1.5846
SDS - Na ₂ CO ₃ - Na ₂ SO ₄ - CV - Lipase	1023.382	1553	4.0466	0.4023	3.9494	72.666	53.873	1.5903
SDS - Na ₂ CO ₃ - Ethanol - CV	1024.957	1556	4.0297	0.4015	3.9633	52.212	55.365	1.5948
SDS - Na ₂ CO ₃ - Ethanol -CV - Lipase	1026.859	1559	4.0068	0.4003	3.9822	62.687	58.870	1.6009

10 mM and the lipase concentration was taken as 1×10^{-4} g/ml. It was found that the addition of SDS with dye removed the colour slowly, but when lipase was added the colour removal was instantaneous. The same effect was observed by other research worker also.^[9]

The acoustical parameters for detergent- crystal violet dye- lipase are presented in Table 3. When the dye colour is removed, the ultrasonic velocity increases which is found from the data in Table 3. When lipase is added to SDS - CV solution the ultrasonic velocity increases and there is corresponding decreases in adiabatic compressibility and intermolecular free length values. The enzyme lipase enhances the detergent action of SDS. This is also supported by the increase in γ , E and Y values. Thus the detergent action is enhanced by the addition of lipase in the removal of dye colour.

FTIR spectra of SDS builder, fillers, dye and lipase have shown variations, which are due to filler and dye. The variation clearly indicates the presence Alkyl amine, amine Aryl tertiary and sulphur groups. So, the enhancement of detergent action by lipase has been confirmed by FTIR spectrum measurement.

Conclusion

Lipase functions as a bio-detergent. It enhances the detergent action of the common surfactants in the removal of dye colour. This is established by the measurement of the acoustical properties and

surface properties for solutions containing SDS, SDS-builder- filler-dye-lipases solutions.

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Forthcoming Events and Conferences

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16 – 20 April 2012, Durban, South Africa, **18th World Conference on Non-destructive Testing**
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02 - 06 July 2012, Edinburgh, UK, **11th European Congress on Underwater Acoustics**
<http://www.acua2012.com>

08 - 12 July 2012, Vilnius, Lithuania, **18th International Congress on Sound and Vibration (ICSV19)** <http://www.icsv19.org>

11 – 13 September, 2012, Daventry, U.K., **51st Annual Conference of British Institute of NDT**
<http://www.bindt.org>

12 - 15 September, 2012, Granada, Spain **30th European Conference on Acoustic Emission Testing (EWGAE) and the 7th International Conference on Acoustic Emission (ICAE)**
<http://2012.ewgae.eu/>

7 – 10 October, 2012, Dresden, Germany, **2012 IEEE International Ultrasonics Symposium**
<http://www.ieee.org>

19 - 21 November, 2012, Aachen, Germany **Aachen Acoustics Colloquium**
<http://www.aachen-acoustics-colloquium.com/>

17 - 20 March, 2013, Les Arcs, France **Electroceramics for End-users VII (PIEZO 2013)**
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1 - 4 May, 2013, Singapore **3rd International Congress on Ultrasonics (ICU 2013)** concurrently organized with the **32nd International Symposium on Acoustical Imaging (AI 2013)**
[http://www.epc.com.sg/PDF Folder/ICU 2010 Phamplet v1 \(12 Jul 2010\).pdf](http://www.epc.com.sg/PDF Folder/ICU 2010 Phamplet v1 (12 Jul 2010).pdf)

02 - 07 June, 2013, Montreal, Canada **21st International Congress on Acoustics (ICA 2013)**
<http://www.ica2013montreal.org>

21 - 25 July, 2013, Prague, Czech Republic, **2013 IEEE UFFC Joint Symposium**
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