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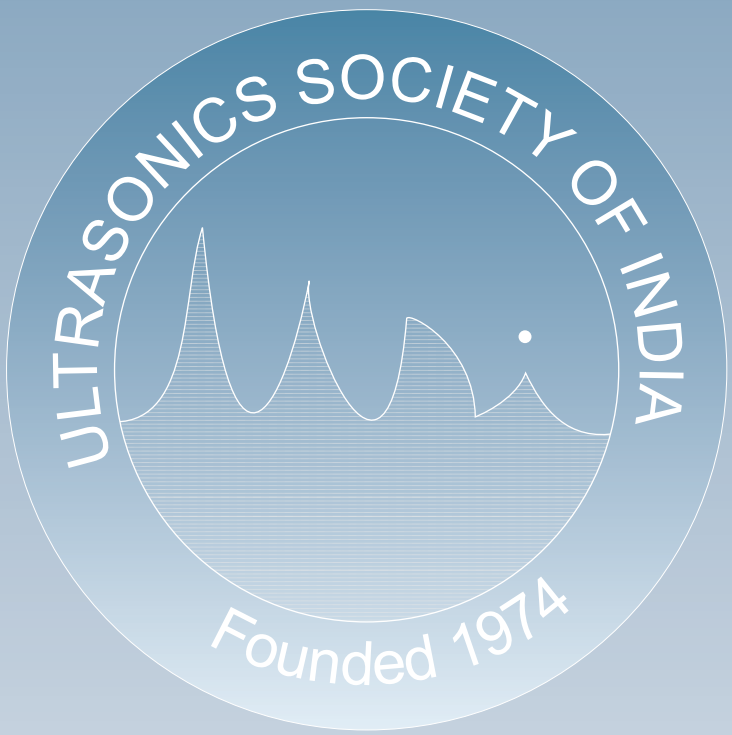

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- Deep Gupta, R.S. Anand and Barjeev Tyagi - Edge preserved enhancement of ultrasound medical images using multiscale ripplet transform based OGS algorithm, *J. Pure & Appl. Ultrason.* Vol **35** (2013) 111-119.
- Mohankumar K,. Supriya M.H, Saseedharan Pillai - Implementation of bicepstral target classifier with support vector machines for noise sources in the ocean, *J. Pure & Appl. Ultrason.* Vol **36** (2014) 3-7.

Dr. M. Pancholi Award for best oral presentation : Mr. Punit Kumar Dhawan, Meher Wan and R R Yadav - "Ultrasonic and elastic properties of one dimensional ZnO nanostructures"

Dr. M. Pancholi Award for best poster presentation : Ms. Aditi Pande, A C Balharpure, S J Sharma and S Rajagopalan -"Touch screen based sing around system for ultrasonic velocity measurement in liquids"

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Characterization of Cu-PVA nanofluids: ultrasonic and thermal properties

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Nanofluids have unique features different from conventional solid-liquid mixtures which have millimeter or micrometer sized particles dispersed in some base fluid. Due to their excellent characteristics, these new types of fluids have attracted wide interest in recent years. It is found that nanofluids have significantly higher thermal conductivity than the base fluids. In this work we focus on the ultrasonic and thermal properties of nanofluids. Nanofluids containing copper nanoparticles with base fluid polyvinyl alcohol (PVA) have been developed in our laboratory. These nanofluids are characterized by UV-Visible spectroscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM). Temperature dependent ultrasonic velocity and ultrasonic attenuation measurements are performed for different concentration of the copper nanoparticles in the PVA. Hot Disk Thermal Constant Analyser is used for the measurement of the thermal conductivity of synthesized nanofluids. Experimental results show that the thermal conductivities of the nanofluids are higher than that of base fluid PVA. The obtained results were analyzed taking into account the ultrasonic and thermal behavior of matrix and particles. Possible mechanism for the enhancement of thermal conductivity of the nanofluids using theoretical model is also discussed.

Keywords: Nanofluids, ultrasonic properties, enhanced heat transfer, effective thermal conductivity, Brownian motion.

Introduction

During the past years a large number of research works have been conducted on manufacturing such materials whose grain sizes are of the order of nanometers. Such nanomaterials have unique optical, electrical, and chemical properties. Nanoparticles when dispersed in liquid remarkably enhance the thermal conductivity of the base liquid. This suspension of nanoparticles in some base fluid is referred as nanofluid. These nanofluid have some unique features that are quite different from the liquid containing millimeter or micrometer sized particles. Nanofluid has higher thermal conductivity, does not block flow channels, and induces a very small pressure drop [1]. Such nanofluids with higher thermal conductivities have many potential applications in the field of heat transfer management. In the cases where the size of the components of the heat transfer devices and flow passages are small, these nanofluids are the best heat transfer fluids. Depending on the types of nanoparticles (metallic/nonmetallic) and base fluid (organic or inorganic), one can get different kinds of nanofluids. Recent interest in nanofluids stimulated from the work of Choi and his coworkers who observed that nanofluids have much higher thermal conductivity than predictable from the effective medium theories [2-8]. In addition, nanoparticles resist sedimentation, as compared to larger particles, due to Brownian motion and interparticle forces and possess much higher surface area (1,000-time) which enhances the heat conduction of nanofluids as heat transfer occurs on the surface of the fluid. Only small amounts of nanoparticles (5 Vol.% or less), can enhance thermal conductivity of the base fluid to a significant value [9]. Nanofluids, produced by dispersing nanoparticles into conventional heat transfer fluids like water, ethylene glycol, poly vinyl alcohol *etc.*, are proposed as the next generation heat transfer fluids

due to the fact that their thermal conductivities are significantly higher than those of the base liquids [10]. Hong *et al.* suggested that suspensions containing small nano-particle clusters are more efficient in improving thermal conductivity than that of individual dispersed nanoparticles because the clustered nanoparticles may provide a longer path for heat transfer [11]. Nanofluids containing a small amount of metallic or nonmetallic nanoparticles like Cu [12], Al_2O_3 [13], CuO [14], SiC nanoparticles or nanotubes [15] are synthesized and studied by several research groups. It has been found that the thermal conductivity of a nanofluid having 0.3vol% Cu nanoparticles dispersed in ethylene glycol increased by up to 40% over that of pure ethylene glycol [16]. Cu nanofluids can be prepared by dispersing Cu nanoparticles into base liquids either by step-by-step method or by one-step methods that combine the preparation of nanoparticles with the preparation of nanofluids, so that the processes of drying, storage, transportation, and redispersion of Cu nanoparticles are avoided hence agglomeration of nanoparticles may not take place in this method. Ultrasonic characterization of the nanofluids is important because ultrasonic methods are nonradiative, nondestructive, cost effective, simple and useful in online characterization demand. Polymers have been found to effective stabilizers of colloidal metal nanoparticles. Among the polymers available, PVA is widely used because of its chemical stability and dissolubility in many solvents. Due to its affinity towards metals, PVA polymer was often used to obtain stable dispersions of metals nanoparticles synthesized by many methods, such as irradiation, reflux, and addition of chemical reductants. Recently, Yadav *et al.* [17-20] have measured ultrasonic attenuation in nanofluids having various concentrations and correlated it to thermo-physical property of the nanofluid. Biwa *et al.* studied the ultrasonic wave attenuation and ultrasonic velocity in suspensions containing metallic or non-metallic solid particles of micrometer and millimeter size, aiming to find out the mechanism that can be correlated to particle size, concentration and mechanical properties of the constituents [21].

Experimental

$CuCl_2.2H_2O$ and PVA were received from M/s Merck Chemicals & Reagents. The freshly prepared homogeneous colorless solutions of PVA in water have been used for synthesis of nanofluids containing Cu nanoparticles. 1.0 M aqueous solution of $CuCl_2.2H_2O$ has been used to derive the nanofluids of Cu-PVA having concentrations of Cu contents 0.2, 0.5, 1.0 and 2.0 wt% in total solution using chemical route. We have made ultrasonic measurements to determine the ultrasonic velocity and ultrasonic attenuation at different temperatures and at different nanoparticle concentration in the polymeric fluids for their characterization. The absorption spectrum of nanofluids was recorded using a Lambda 35, Perkin-Elmer double beam UV-visible absorption spectrometer, using a 1 cm quartz cell. A thick film of the nanofluid was dried on the glass plate for X-ray diffraction analysis. XRD measurement was done by X'Pert-Pro, PANalytical (with CuKα radiation λ =1.5406 Å) operating at room temperature. The particle size and its distribution were analyzed with E.M.-C.M.-12 (Philips) transmission electron microscope operating at 200 KeV.

Results and Discussion

When adding aqueous solutions of $CuCl_2.2H_2O$ to a PVA solution in water, polymer complex forms by a redox reaction of $CuCl_2.2H_2O$ with the PVA molecules of refreshed reactive nescent surfaces caused during the processing using the mechanochemical attritions under heating conditions of the solution. The UV-visible spectrum shows strong absorption peaks at 588 nm for 0.5 wt% Cu-PVA nanofluids [Fig. 1]. The sharp absorption peak indicated narrow size distribution of Cu metal nanoparticles in PVA. All the nanofluid samples showed symmetrical peaks due to the surface plasmon resonance of metal nanoparticles. The peaks typically

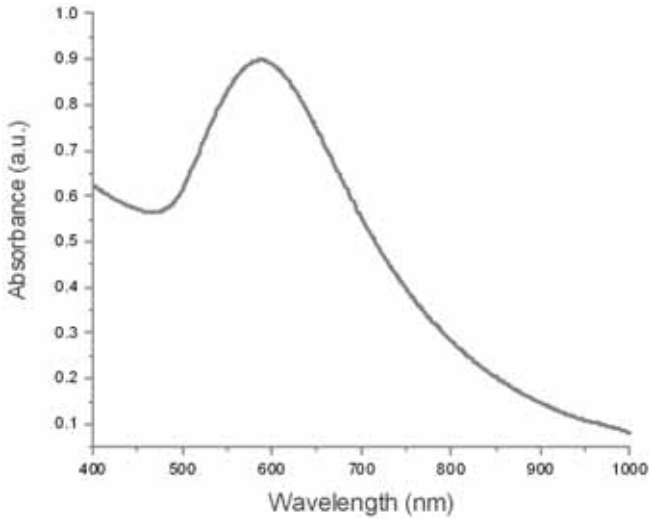

Fig. 1 UV-Visible spectrum of 0.5 wt % Cu nanoparticles-PVA suspension

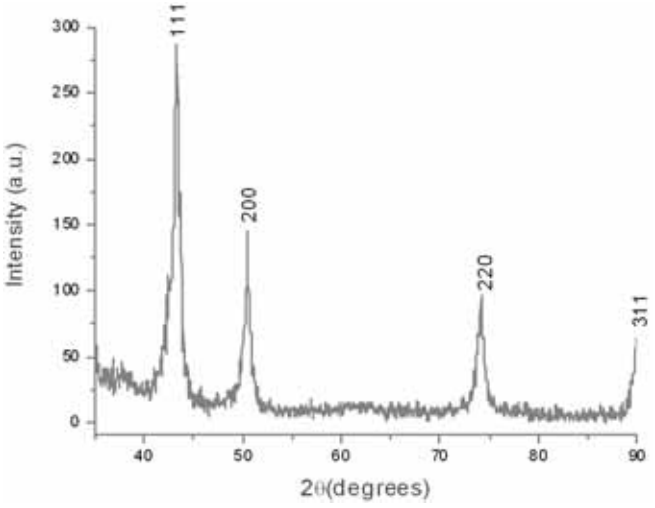

Fig. 2 XRD pattern of 0.5 wt % Cu nanoparticles- PVA suspension

represent the formation of small metal nanoparticles in the solution. The UV-visible spectrum suggests that Cu salts have been reduced by PVA. The XRD analysis of the nanofluids has confirmed the formation of metallic copper nanoparticles in the solution [Fig.2]. XRD results reveal that the Cu metal nanoparticles are cubic crystalline (F_{m3m} space group).

Fig. 3 shows the TEM image of the Cu-PVA nanofluid. The average size is seen to be about 10 nm. The copper nanoparticles are well dispersed in colloidal solution as evinced by TEM micrographs.

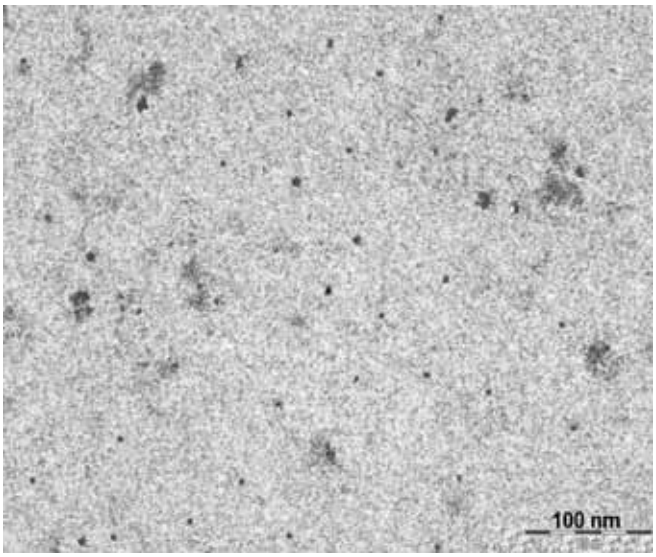

Fig. 3 TEM micrograph of 0.5 wt% Cu nanoparticles- PVA suspension

Figs. 4 and 5 show the temperature dependent ultrasonic velocity and ultrasonic absorption for different samples of Cu-PVA nanoparticles-liquid suspensions respectively.

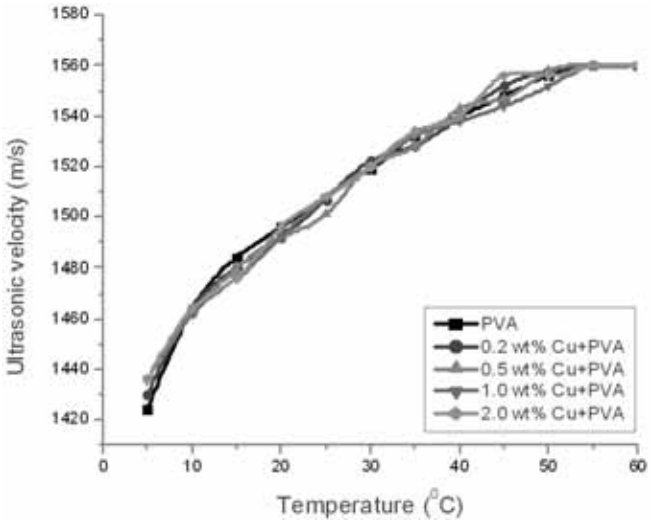

Fig. 4 Temperature dependent ultrasonic velocity in Cu-PVA nanofluids

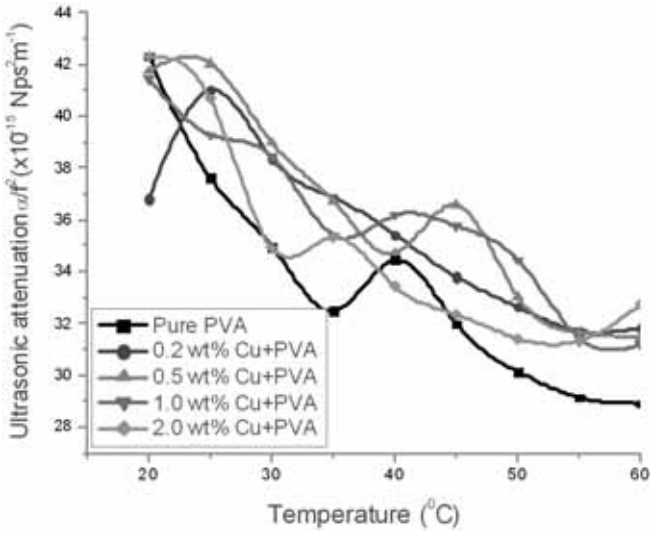

Fig. 5 Temperature dependent ultrasonic attenuation in Cu-PVA nanofluids

The variation of ultrasonic velocity with temperature is almost same for all concentrations of Cu metal nanoparticles. For Cu-PVA, there is no distinct minimum in ultrasonic velocity with temperature. Now the ultrasonic absorption is measured for the Cu-PVA colloids. The measurement is done for different concentration/ temperature of the sample. Fig. 5 shows

that the maximum attenuation appears in 0.5 wt% Cu nanoparticles-suspended in PVA.

In general, as in other materials [22], both the ultrasonic velocity and attenuation are quite sensitive to the particle size, morphology and dispersion of the particles. The effective attenuation in the Cu-PVA colloidal nanofluid can be expressed as $\alpha = \alpha_p + \alpha_m + \alpha_{pm}$ where α_p is the contribution from the Cu-metal, α_m is the counterpart contribution from the polymer matrix, α_{pm} describes the change in the final α-value owing to a macroscopic interaction between the two components in Cu-PVA nano-colloid structure and associated modified thermo-physical properties of the nanofluid. S. Biwa and coworkers [21] analyzed the ultrasonic absorption in millimeter sized particles- reinforced polymers by a differential scheme and found good agreement between the theory and experiments. The wave attenuation in these composites is a complex process where the viscoelastic loss and the scattering loss coexist.

Fig. 6 shows the thermal conductivity of the nanofluid due to dispersion Cu nanoparticles in base fluid PVA.

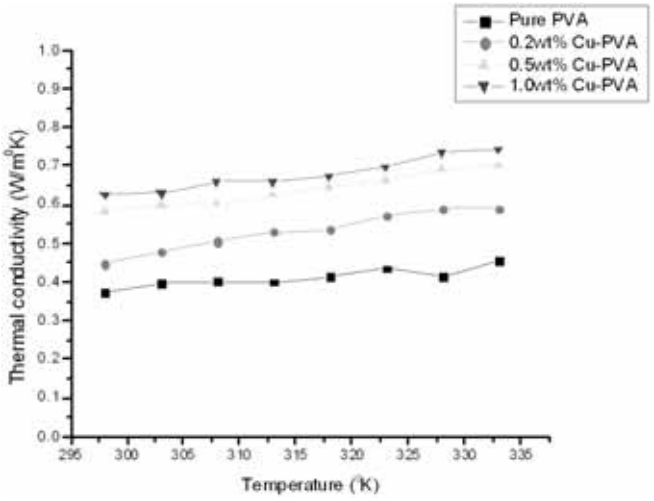

Fig. 6 Thermal Conductivity of Cu-PVA nanofluid at different temperatures

Nanofluids have anomalously high thermal conductivities at very low nanoparticles concentrations [16,23,24]. To date, the exact mechanism of thermal transport in nanofluids is not fully known, and several possible mechanisms based on theoretical models, experiments and previous heat transfer theory have been suggested to describe experimental results on thermal conductivity of nanofluids. Brownian motion of suspended nanoparticles is attributed as one of the key factors of the greatly enhanced thermal conductivity performance and it was not considered in conventional thermal transport theory. U.S. Choi *et al.* proposed the theoretical model that accounts for the fundamental role of dynamic nano particles in the nanofluids [2]. They have derived a general expression for the thermal conductivity of nanofluids involving different modes of energy transport in the nanofluids. The important mode is thermal interaction of dynamic or dancing nano-particles with base fluid molecules. Even though the random motion of nanoparticles is zero when time averaged, the vigorous and relentless interactions between liquid molecules and nanoparticles at the molecular and nanoscale level translate into conductions at the macroscopic level, because there is no bulk flow. Moreover, the thermal conductivity model not only captures the concentration and temperature dependent conductivity, but also predicts strongly size-dependent conductivity. As we have seen the thermo-elastic ultrasonic attenuation (dissipative type attenuation) is directly proportional to the thermal conductivity of the composite and the attenuation due to scattering for the nanoparticles is almost negligible. Further, the observed anomalous enhancement in thermal conductivity is also justified with another model by Das *et al.* [25], which is the composite model consisting stationary particle model approach and moving particle approach to calculate effective thermal conductivity of nanofluids. In stationary particle model approach, it is assumed that the heat conduction happens by two paths as through highly conducting nanoparticle medium and through liquid medium. This assumption explains the thermal conductivity enhancement due to particle concentration. According to this assumption, the thermal conductivity enhancement will be directly proportional to ratio of thermal conductivities and volume fraction of nanoparticles and liquid matrix and inversely proportional to particle radius. From Das *et al.*, it can be written as :

$$\left(\frac{K_{eff}-K_m}{K_m}\right) = c\bar{u}_p \frac{\varepsilon r_m}{K_m(1-\varepsilon)r_p}$$ where $(K_{eff} - K_m)/K_m$ is enhancement factor of thermal conductivity in nanofluids. It is also evident from this model that the thermal conductivity of inhomogeneous liquid mixtures is inversely proportional to viscosity of the liquid medium. Since the viscosity of the liquid medium *i.e.*, base fluid decreases with increase of temperature and results in further increase in particle velocity and thus thermal conductivity. This model is better in molecular

size regime and may not be considered better when the concentrations of the nanoparticles are much higher so that the inter-particle interactions become important. Thus it may reflect better correlation with our experimental data for smaller particles. As we have used small amounts of nanoparticles in preparation of nanofluids, the fluidic properties of liquid are almost unaffected for the easy flow of liquids in order to better transfer of heat from one place to other. The low dimensional copper nanoparticles reinforced nanofluids have much higher thermal conductivity and stability for heat transfer applications because of smaller dimension of nanoparticles. Therefore, we predict that the effective enhanced thermal conductivity of the nanofluid has such an impressive effect as the excess attenuation on the total ultrasonic attenuation behaviour.

Conclusion

1. Synthesis of Cu-PVA nanofluids have been carried out successfully by a novel chemical route.
2. Characterization techniques such as UV-visible, XRD and TEM confirm the formation of monodispersed nonagglomerated Cu nanoparticles in PVA.
3. Ultrasonic absorption in nanofluids shows interesting behavior.
4. Hot disk thermal constant analyzer result reveals that the dispersion of Cu nanoparticles in PVA enhances its thermal conductivity significantly.
5. Experimental results show that the behavior of ultrasonic attenuation is well related to the enhancement in the thermal conductivity of PVA due to Cu nanoparticles.
6. These nanofluid samples can be used successfully for any heat transfer management systems in industrial applications.

Acknowledgments

The authors (Giridhar Mishra and R.R. Yadav) are thankful to Department of Science and Technology, Govt. of India (DST project no. SR/S2/CMP-0069/2006) for the financial support to carry out the work.

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Effect of thickness of epoxy encapsulation material on the performance of underwater tonpilz transducer

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Electro-acoustic transducers capable of converting electric energy to acoustic energy and vice versa are critical elements in Sonar systems. Among different types of electro-acoustic transducers Tonpilz transducer is widely used due to their ability to operate in both transmitting and receiving mode and generation of directional high acoustic power. Typically tonpilz transducers are encapsulated by a visco-elastic material when used in underwater applications. The primary function of encapsulation material is to protect the transducer from water ingression and physical damage without affecting significantly the acoustic transmission and reception properties, thereby influencing efficiency and reliability of transducers. In view of these, epoxy elastomers are widely used for encapsulation of tonpilz transducers. The term epoxy, epoxy resin or epoxide refers to a broad group of reactive compounds that are characterized by the presence of an oxirane or epoxy ring. For applicability and suitability of epoxy for a particular underwater application, its compositions and encapsulation thickness are the crucial parameters. In this paper the effect of the variation of encapsulation thickness of epoxy on the transmitting voltage response (TVR) and free field sensitivity (FFS) of a tonpilz transducer designed for underwater applications are presented.

Keywords: Electro-acoustic transducer, acoustic impedance, epoxy, TVR and FFS.

Introduction

Electro-acoustic transducers capable of converting electric energy to acoustic energy and vice versa are widely used in many underwater applications starting from civilian to military such as ocean depth sounder, sea bottom profiler, underwater explorations, sea mines, decoys, torpedo homing *etc*. The designs and configuration of above transducers depend upon the nature of application and required output. Among different designs of transducers Tonpilz (German for "singing mushroom") design is widely used due to their ability to operate in both transmitting and receiving mode and generation of directional high acoustic power apart from their simplicity in fabrication. In this design a piezoceramic stack polarized in thickness mode is sandwiched between a light head mass and a heavy tail mass and the device resonates like a spring-mass system when an electrical voltage is applied to the ceramic section along poling direction. The transducer is compressively prestressed by placing a bolt through the center of the ceramic stack to prevent the ceramic from shattering during extensional phase of vibration. The head is shaped like a frustum of cone for gradual transition and higher transfer of acoustic energy from piezoceramics having high acoustic impedance to the water having low acoustic impedance. The details of design of a tonpilz transducer are given elsewhere [1, 2, 3]. During operation the tonpilz transducers are encapsulated with a polymeric material. The primary function of encapsulation material is to protect the transducer from water ingression and physical damage without affecting significantly the acoustic transmission and reception properties. Apart from this, other important considerations for transducer encapsulation materials are : (a) close acoustic impedance matching with seawater for higher transfer of acoustic energy between transducer and surrounding water medium; (b) low mechanical loss tangent (tan δ) within the frequency ranges of interest to minimize the loss of acoustic energy in the form of heat; (c) low water absorption and water permeability; (e) room temperature curing; and (f) low insertion loss during the transmission of acoustic energy

through the material within the frequency range of interest; (g) sufficient strength to withstand hydrostatic/ hydrodynamic pressure exerted on it depending upon the depth of application and nature of underwater system where the transducer is fitted; (h) resistance to sea water ageing [4,5]. Upon analyzing above critical parameters it is evident that for better reliability and efficiency of transducer, the compositions of the material and encapsulation thickness are the crucial parameters. Composition decides the acceptability of the material in general for encapsulation whereas thickness influences depth of operation and transmitting and receiving performances of the transducer. In view of these, a number of epoxy materials from different manufactures have been widely used to encapsulate underwater tonpilz transducers. Though the properties of these epoxy materials are adequate in general for underwater applications, they are to be optimized for applications involving a transducer designed to have desired transmitting and receiving response within a particular frequency range and to operate at a certain depth. In this paper the effect of thickness variation of in-house developed epoxy on the transmitting voltage response (TVR) and free field sensitivity (FFS) of a tonpilz transducer designed for SONAR applications is reported.

Material and Method

Design of Tonpilz Transducer

A tonpilz transducer to be operated at required resonance frequency is designed. The transducer has an alumina head, a stack of piezoceramic rings made up of CEPZOID IV S (a Navy type I material by M/s Concord Electro Ceramic Industries, India), brass tail and a stress bolt of Beryllium-Copper (Be-Cu) alloy. The Finite Element Package ATILA (Analysis of Transducers by Integration of LAplace equation) [6] is used to optimize the dimensions and shapes of each component. The piezoceramic rings are interconnected mechanically in series and electrically in parallel. The whole structure is then pre-stressed through a bolt by applying the required torque.

Epoxy encapsulation material

The epoxy polymers are basically polyethers. The term epoxy, epoxy resin, or epoxide refers to a broad group of reactive compounds that are characterized by the presence of an oxirane or epoxy ring. This is represented by a three-member ring containing an oxygen atom that is bonded with two carbon atoms already united in some other way. Epoxy resin is prepared from Epichlorohydrin and a polyhydroxy compounds like bisphenol-A, glycols, glycerols, cresol, resorcinol etc. The epoxy resins obtained through these reactions will be either highly viscous liquids or high melting solids. The epoxy resins can be further cured with substances such as amines, polysulphides and polyamides. Epoxy materials exhibit a great range of properties (from soft to hard) which leads to a great versatility in application. This is mainly due to good adhesive properties, mechanical properties, low expansion coefficients and low viscosity. Epoxy materials can be employed in a typical array as inter-element, passive intra element filler between active transducers, backing material and as acoustic window material. Epoxy is the material of choice for underwater acoustic transmission applications as its acoustic impedance can be made to match the acoustic impedance of sea water. Acoustic impedance can be modified over a broad range for epoxy material by changing the resin (prepolymer) to curing agent ratio in the composition [7-10].

An epoxy material composition is developed for encapsulation of underwater electro-acoustic transducer. It is a two component room temperature cure system. The component one is a prepolymer of Cresyl glycidyl ether and it is prepared by the reaction between Cresol & Epichlorohydrin. It is a liquid resin having viscosity of 225 Pa.s. The component two is curing agent or catalyst and it is an aliphatic amine *i.e.,* Triethylene Tetramine (TETA). It is black colour liquid having viscosity of 25 Pa.s. The prepolymer resin and curing agent mixed in the ratio of 1:1 for desired properties. Epoxy Resin/Curing agent is a black, filled epoxy adhesive and it bond well to wide variety of substrate.

The acoustic properties of epoxy which are of greatest interest to transducer encapsulation are sound speed within the material and its acoustic impedance defined as density multiplied by sound speed. The acoustic impedance is the opposition to displacement of its particles by sound waves and also an influencing factor for transmission or reflection of sound waves when it travels through different mediums. Maximum transmission of sound energy occurs if the acoustic impedance of the two media is equal. The sound speed within the developed epoxy is measured to be 2250 m/s at room temperature using a ultrasonic thickness gauge Using this sound speed and density (1200 kg/m^3) of developed epoxy, the acoustic impedance of material is 2.7 MRayls (Kg.m^{-2}.s^{-1}) which is a close match with

seawater (the acoustic impedance of seawater is 1.53 MRayls at room temperature). The acoustic transparency of the material is determined by insertion loss and echo reduction properties.

Insertion loss (IL) in dB = 20 log (Incident sound pressure /Transmitted sound pressure).

Echo reduction(ER) in dB = 20 log (Incident sound pressure /Reflected sound pressure)

For better acoustic transparency the material should have low insertion loss and high echo reduction values within the frequency range of interest. The IL and ER values obtained for epoxy from the measurement by panel method are less than 2dB and greater than 15 dB respectively in the frequency range of interest. The tensile testing of the materials was carried out in a Universal Testing machine (Hungta, Taiwan) according to ASTM D 412 and is found to be 10.3 MPa. The hardness measured as per ASTM D-2240 standard with the help of Universal Hardness tester (Baressis, Germany) is found to be 70 Shore-A. Materials resistance to sea water absorption determined as per ASTM D-471 standard is less than 1%.

Experimental

The resonance and anti-resonance frequencies, impedance, capacitance and dissipation factors of fabricated tonpilz transducer are measured in air using an impedance analyzer. The fabricated transducer is then fitted in special aluminum housing for encapsulation and further testing. Encapsulation of the developed epoxy is done by cold casting technique. Both prepolymer resin and curing agent taken separately in to a clean container. Both the chemicals were degassed under vacuum. The prepolymer resin and curing agent weighed as per mixing ratio and mixed thoroughly with the help of stirrer. The mixed chemicals were degassed under vacuum. The mixture was immediately poured onto the head portion of transducer fitted in the housing using die assembly. Material is cured at room temperature for 24 hours. Then demoulding of item is done. After one week of casting, the item is subjected for further tests. In this way transducers are encapsulated with epoxy materials of thickness of 5 mm, 10 mm, 15 mm and 20 mm.The transducer fitted in the housing before encapsulation and after encapsulation is shown in fig 1.

The transmitting and receiving performances such as TVR and FFS of the encapsulated transducers are measured in the acoustic tank facility using tone-burst method under free-field conditions over a desired frequency range [11]. TVR stands for transmitting voltage response of the transducer and is defined as the on-axis sound pressure p at 1meter produced by a drive voltage V of 1 Volt and referenced to 1µPa. In decibel form it is expressed as TVR (dB re 1µPa/V at 1 m) = 20 $\log_{10}$ (p/V). Similarly FFS stands for free field sensitivity of transducer is the ratio of the electrical output voltage, with output open circuited, to the applied pressure. In decibel form it is expressed as FFS (dB re 1V/µPa) = 20 $\log_{10}$ (V/p).Comparison calibration method with NI hydrophone calibration system is used to determine the transmitting and receiver properties of the encapsulated transducers. ITC-1032 hydrophones are used as the standards.

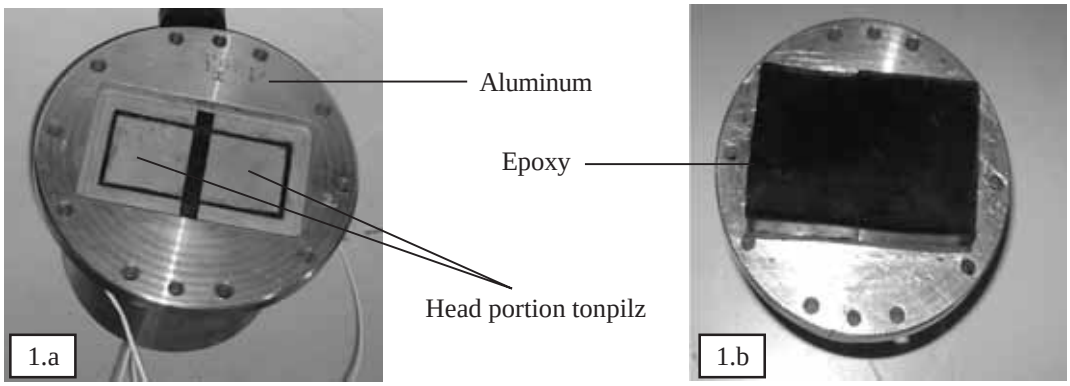

Fig. 1 Encapsulation of tonpilz transducer with epoxy. Two number of designed tonpilz transducer is fitted in an Aluminum housing. The head portions of the transducers are separated from each other and from housing by rubber grids for electrical isolation as shown in fig.1.a. The transducer after Epoxy encapsulation is shown in fig.1.b.

Results and Discussion

The measured Transmitting Voltage Response (TVR) and the Free Field Sensitivity (FFS) response as a function of frequency are shown in fig.2 and fig. 3 respectively.

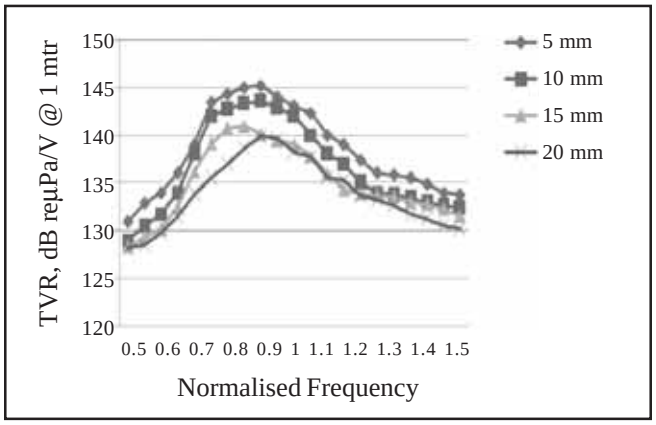

Fig. 2 Effect of epoxy encapsulation thickness on the transmitting response of the tonpilz transducer designed for SONAR application when tested in water. The thickness of in-house developed epoxy is varied from 5 mm to 20 mm in steps of 5 mm. The change in TVR of the transducer is shown in figure. Peak TVR reduces form 145.2 dB for 5mm Epoxy thickness to 139.9 dB for 20 mm Epoxy thickness.

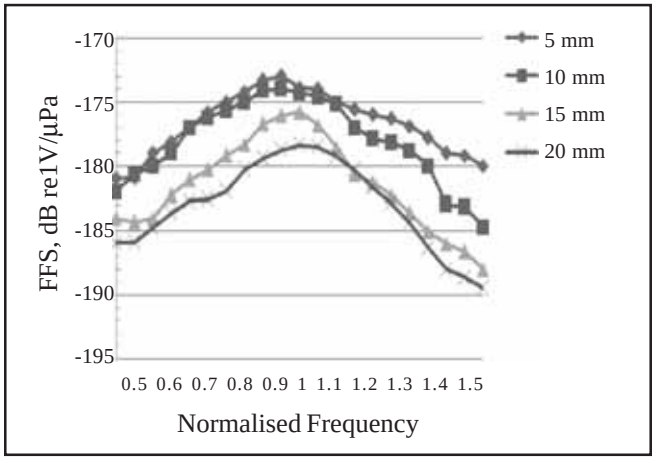

Fig. 3 Effect of epoxy encapsulation thickness on the receiving response of the tonpilz transducer designed for SONAR application when tested in water. The thickness of in-house developed epoxy is varied from 5 mm to 20 mm in steps of 5 mm. The change in FFS is shown in figure. The peak FFS decreases from -173 dB at 5 mm Epoxy thickness to - 178.4 dB at 20 mm of Epoxy thickness.

The test results validate the effectiveness of the developed epoxy as encapsulation materials for the designed tonpilz transducer. There is a reduction of peak TVR values from 145.2 dB to 139.9 dB is observed when thickness is increased from 5mm to 20mm. Similarly reduction of peak FFS values from -173 dB to -178.4 dB is observed. These reductions are attributed to the acoustic impedance mismatch at the interface of epoxy and water, insertion loss and mechanical loss occur in the epoxy material which increase as thickness of the material increases and increase in mass loading on transducer due to epoxy material which results in decrease in vibration amplitude of tonpilz transducer.

Conclusion

An epoxy material to be used for encapsulation of a designed tonpilz transducer is developed. Acoustic impedance of the material was calculated as 2.70×10^6 $Kg.m^{-2}.s^{-1}$ which is close to the acoustic impedance of sea water (1.53×10^6 $Kg.m^{-2}.s^{-1}$). Insertion loss values are less than 2 dB and echo reduction values are more than 15 dB throughout the frequency range of interest. The designed tonpilz transducer is then encapsulated with the developed Epoxy of thickness from 5 mm to 20 mm with a step of 5mm and its acoustic responses in water are measured. The results indicate that there is a reduction of approximately 5.3 dB in transmitting sensitivity and 5.4 dB in receiving sensitivity. Also epoxy of particular thickness has to withstand the hydrostatic pressure due to use of transducer at required depth. Hence the exact thickness of epoxy can be decided as per the transducer's TVR, FFS requirements, resonance frequency in water and the depth of operation.

Acknowledgements

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Ultrasonic study of solvent extractant in nuclear technology

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The experimental data of ultrasonic velocity and calculated values of density are used to study the different interactions in the extractants tri-n-butyl phosphate (TBP) with kerosene. The temperature of the system is maintained 303 K and the frequency used to measure the ultrasonic velocity are 1MHz, 3MHz and 5MHz. This study involves evaluation of different thermo-acoustic parameters along with the excess properties, which are interpreted in the light of inter-molecular interaction between polar extractants with non-polar diluents.The variation of these thermo-acoustic parameters with concentration and frequency insight the information regarding the extraction process of some rare earth elements (REEs) like yttrium, lanthanum.

Keywords: Solvent extraction, TBP, molecular interactions, intermolecular free length, acoustic impedance, isentropic compressibility

Introduction

The characterization and identification of different interaction in binary mixtures is an important step in liquid-liquid extraction technology. Liquid-liquid solvent extraction reagents used in several nuclear technological areas such as purification of reactor materials, radio nuclide production and the recovery of many nuclear material such as Thorium, Uranium and Plutonium etc. Solvent extraction technology is commonly used in many industrial processes and separates compound based on their relative solubilities in two different immiscible liquids. The knowledge of acoustic properties reveals the presence of different molecular interactions between the component molecules in the liquid mixture. The presence of molecular interaction in binary mixtures of nuclear extractants with non polar solvents identifies efficient modifier/diluents to be used in the solvent extraction process in the preparation of nuclear reactor materials. In extraction process it is generally observed that a third phase appears at the interface of organic and aqueous phase [1] which reduces the extraction efficiency of extractants in its pure form. Thus the mixing of the extracts with suitable diluents alters the physical properties of the extracts and helps to improve the extraction efficiency. As a part of our ongoing work, it is an attempt to study systematically the physicochemical behavior of TBP with kerosene by evaluating different thermo-acoustic parameters like isentropic compressibility (β), intermolecular free length (L_f), acoustic impedance (Z), molar volume, surface tension and the relevant excess data. The review of literatures [2-4] shows that many attempts have been made to compute ultrasonic velocity in different binary mixture at different temperature but such study with variation of frequency is rare. Thus an attempt has been made to study and characterize the different intermolecular interaction [5-6] present in binary mixture system like TBP and Kerosene. Finally it is found that the extraction efficiency of REEs is also increases with mole fraction of extracts in diluents with minimum optimum value of extractants.

Material and Method

High purity and analytical grade samples of TBP 99.0 % (GC) and Kerosene 99.0 % (GC) are procured from SD chemicals India. The entire chemical used in the study are purified by standard procedure [9-10] and redistilled before use. To minimize the contact of this deliquescent liquid with moist air, the product was kept in sealed bottles in desiccators. The purities of the sample were confirmed by GLC. Binary mixtures were prepared by mass in air tight bottles. The mass measurements were performed on high precession digital balance with an

accuracy of ± 1 mg. The uncertainty in mole fraction was ± 0.001.The densities of pure liquids and their mixture were determined by using double arm pyknometer with accuracy of the order of ± 0.01 kg/m^3

Experimental Details

The ultrasonic velocity of the above liquids and their mixtures were measured using multi-frequency ultrasonic interferometer operating at different frequencies like 1 MHz, 3 MHz and 5 MHz. The accuracy in the measurement of ultrasonic velocity was within ± 0.01 ms^{-1}. The working principle used in the measurement of velocity of sound through medium was based on the accurate determination of the wave length of ultrasonic waves of known frequency produced by quartz crystal in the measuring cell [11-13].The temperature of the solution was controlled by circulating water at a desired temperature through the jacket of double walled cell within ± 0.01 K using a constant temperature bath and the temperature was monitored with a platinum resistance thermometer with an accuracy of ± 0.001 K.

Theory

The experimental measured values of ultrasonic velocity and computed values of density are used to compute acoustic parameters such as isentropic compressibility (β), intermolecular free length (L_f), acoustic impedance (Z) and surface tension and their excess values. The above acoustic parameters are determined with the help of the following relationship.

$$\text{Isentropic compressibility } (\beta_s) = \frac{1}{\rho C^2} \quad (1)$$

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

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

and their excess values are calculated as :

$$\left(Y^E\right) = Y_{mix} - \left(X_A Y_A + X_B Y_B\right) \quad (4)$$

where X_A, X_B, Y_A, Y_B and Y_{mix} are mole fraction, isentropic compressibility, inter molecular free length ,acoustic impedance of kerosene, TBP and mixture respectively. The constant k is temperature dependent which is given as [93.875 + (0.375T)] × 10^{-8} as per literature [4] and T being the absolute temperature.

Results and Discussion

Experimentally determined ultrasonic speed and measured density were used to calculate isentropic

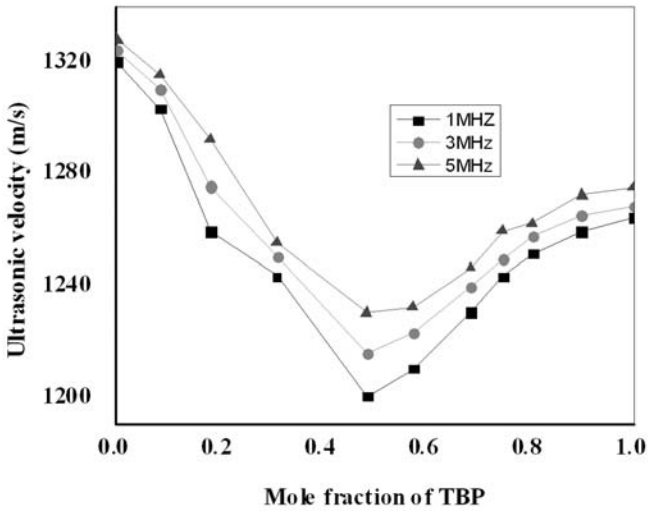

Fig. 1

compressibility (β), intermolecular free length (L_f), acoustic impedance (Z) and their deviated values using the standard relations with accuracy up to third decimal digit. The variations of these parameters with entire concentration range of TBPat different frequency for constant temperature are displayed graphically in Fig.1 to Fig.4. The Fig.1 shows the variation of ultrasonic velocity in binary mixture of kerosene with mole fraction of TBP which is not linear. It is seen that the ultrasonic velocity decreases then increases with mole fraction of TBP, depending on the ultrasonic velocity value of second component in the entire sample. The effect of adding a non-polar second component is primarily to disrupt the dipolar interactions of the first component.

This may be due to self-association of the solvent molecules and a very weak dipole-induced dipole interaction between the component molecules, which is concentration dependent [7]. Further, in this binary system the interaction becomes weak with increase in frequency from 1 MHz - 5 MHz for which the ultrasonic velocity is increases with increase of frequency due to thermal agitation of component molecules. As isentropic compressibility (β) varies inversely with C^2, the trend in isentropic compressibility with concentration is the reverse of the trend in ultrasonic velocity with concentration. Further, the plots of isentropic compressibility with concentration of TBP are nonlinear suggesting that these systems are deviated from the ideal ones. The variations in isentropic compressibility values with concentration indicate that the strength of induced dipole-induced dipole interactions is concentration dependent. The variation of ultrasonic velocity in a solution depends upon

the increase or decrease of intermolecular free length after mixing the components.

The plot of deviated compressibility and deviated intermolecular free length verses mole fraction of acetone in the binary mixture of TBP with Kerosene are shown in Fig. 2 and Fig. 3. It is clear from the profiles that the β^E and L_f^E of the mixture increases negatively for mole fraction of TBP. It was reported that the negative excess compressibility [7] is an indication of strong hetro-molecular interactions in the liquid mixtures which are attributed to charge transfer, dipole-induced dipole, dipole-dipole interactions and hydrogen bonding. With increase in frequency, as the polarity is no longer observed, the moment of the molecule is due to intermolecular gap. So the intermolecular free length is less in high frequency range 3 MHz and 5 MHz for which the molecules are able to move freely for which the intermolecular free length sharply increases up to 50 mole % of TBP and then decreases in pure TBP state as the interaction between the TBP molecules increases.

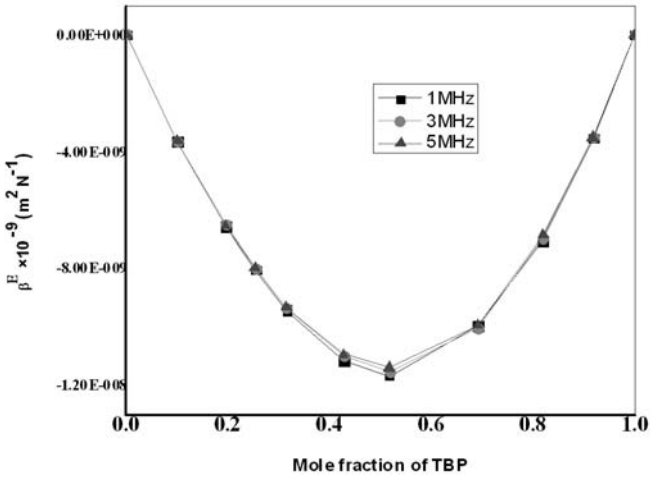

Fig. 2

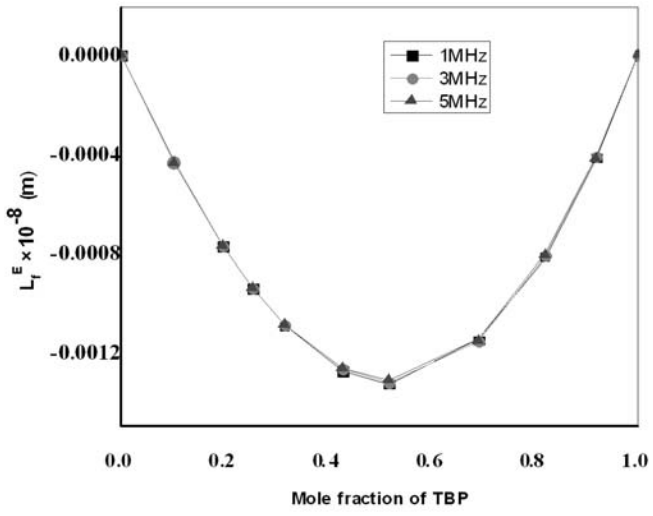

Fig. 3

The variation of β^E and L_f^E are also supported by existence of some specific interaction like excess values of acoustic impedance Z^E. The variation of Z^E as shown in fig .4 in the system reveals that dispersion is more prominent in the systems but the less magnitude of Z^E suggests that there is possibility of strong dipole-induced dipole type of interaction acting between system components. From the nature of the profile it is very clear that in TBP and kerosene system the magnitude of Z^E is appreciably more negative suggesting the fact that the dispersion is more prominent and having strong dipole -induced dipole interaction in system. Again considering the effect of frequency it is also informative that with increase of frequency the values of Z^E goes on increasing leads to conformation that the interactions goes on increasing.

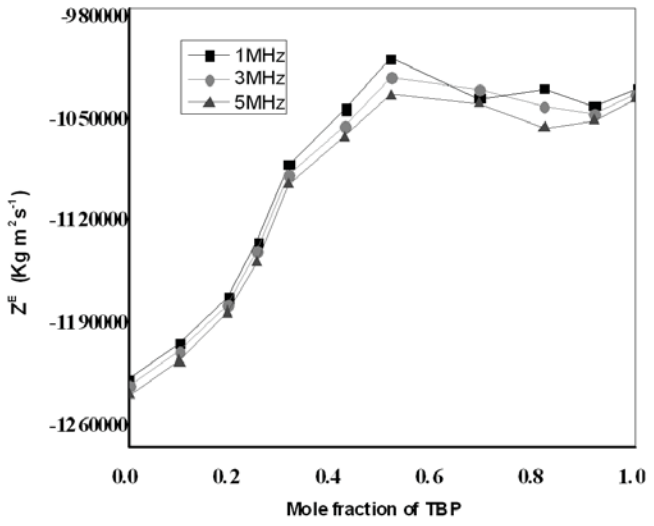

Fig. 4

Conclusion

Thus it can be concluded that the interaction of TBP kerosene is stronger in low frequency as is observed in different acoustic parameters for different frequencies. The dependence of ultrasonic velocity and other derived parameters on composition of the mixture is indicative of the presence of molecular interactions. The sign and magnitude of excess parameter of the mixture and their variations with frequencies reveals that the extent of interaction decreases with increase in frequency. When the concentration of kerosene decreases and TBP

concentration increases there is more than one type interaction like dipole-dipole ,dipole-induced dipole, dispersion force may appears in the mixture which basically responsible for such peculiar variation.Thus the variation of different acoustic parameters with frequency indicates that the in characterization of different intermolecular interaction frequency plays vital role and the mixture is used for extraction process nuclear material in nuclear technology.

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An analysis of acoustical and thermodynamical properties of calcium and ammonium nitrates in non-aqueous media- an ultrasonic study

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Calcium nitrate and ammonium nitrate solutions in methanol, ethanol and isopropanol have been studied ultrasonically using a variable path ultrasonic interfometer working at 2 MHz. The apparent molar compressibility, isentropic compressibility, intermolecular free length, specific acoustic impendence, molar sound velocity and solvation number have been evaluated and discussed. Bachem's relation is found to be obeyed. Constants A and B of this relation in various alcohols have also been determined

Keywords: Sound velocity, Bachem's relation, nastic impedance, solvation number.

Introduction

In recent years, increased attention has been directed towards the ion-solvent interactions at infinite dilution. In very dilute solution, ions may be considered as point charges, but as the concentration increases, the finite size of ion becomes important and the limiting model of Debye-Huckel ceases to be valid for electrolyte solutions. Above certain concentration, ion-solvent, ion-molecule interactions and excluded volume effect start influencing the concentration dependence of most thermodynamic functions. The solvation of ions reduces the activity of available solvent molecules and the finite volume if ions causes interactions between the charge of one ion and the cavities formed in the solution by other ions in a way similar to the origin of interactions between the ions and non-electrolytes. In addition to these interactions, the charges in the structure of solvents, brought about by the ions, often play a predominant role in electrolytic solutions. Only a few papers have appeared on ultrasonic study of non-aqueous solution out of which the work of Bhat and Shivkumar[1], Sinha and Srivastava[2], Ramna et al.[3], Dhanraju et al.[4] and Prasad et al.[5-6] are noteworthy.

The Calcium ion has a radius of 0.99Å which is much less than that of ammonium ion and due to the higher charge density, calcium nitrate has a tendency to produce greater structural changes in solution than ammonium nitrate. The acoustic and apparent molal properties of calcium nitrate and ammonium nitrate in a alcoholic solutions can furnish interesting information regarding ion-solvent interactions. With this fact in view, an attempt has been made to study ultrasound velocity, isentropic compressibility, intermolecular free length, molar sound velocity, acoustic impedance, apparent molal isentropic compressibility, solvation number, the applicability of garnsey and Bachem relations for the solution of Calcium nitrate and ammonium nitrate in methanol, ethanol and isopropanol.

Experimental Details

Calcium nitrate and ammonium nitrate (B.D.H., AR) were used for the preparation of salt solutions in alcohols Calcium nitrate was fused and cooled in a desicator and lumps of the fused salt were powdered and reheated in a glass vial up to 150°C for about two hours, then cooled and weighted. The process was repeated until weighted became constant and then it was kept in vacuum desicator for use. All the solvents namely methanol (E Merck), ethanol (BCPW) and isopropanpl (E Merck) used in present study were further purified using standard procedures[7]. The solutions were prepared by dissolving an accurately known weight of the salt in the liquid and kept for some time in a thermostated bath. The ultrasonic velocity was measured with an variable path ultrasonic interferometer[8] at 2 MHz with an accuracy of 0.2 ms^{-1}. The temperature was controlled by a thermostat with an electronic relay controlling the flow of water with an

Table 1 –Comparison of experimental values of density and viscosity with literature[9]

Values of pure component liquids at 303.15K

Component liquids	Density (ρ) × 10^{-3} (kg m^{-3})		Viscosity (η) × 10^{3} (cP)	
	Experimental	Literature	Experimental	Literature
Methanol	0.7819	0.78186	0.510	0.510
Ethanol	0.7808	0.78097	1.003	1.003

accuracy of 0.01°C. The density was measured with a double walled pyknometer and and single pan electrical balance with accuracy of the results 0.01 g/ml^{-1}. Double distilled water and benzene were used for the calibration of pyknometer. The reliability of the experimental data may be ascertained by comparing the densities of pure organic liquids as obtained in present study with their values as per literature[9] as presented in Table 1 which are in close agreement with each other.

Theory

In an electrolytic solution, the ions are surrounded by solvent molecules and these are firmly bound and oriented towads the ions. This envelope is known as the primary solvation sheath and within this region the solvent molecules are immobilized. The orientation of the solvent molecules around the ions is attributed to the influence of the electrostatic field of the ion and thus the internal pressure increases and the primary effect of dissolving an electrolyte is to lower the compressibility of the solvent, *i.e.* solution becomes harder to compress. The increase in the internal pressure due to electrostatic field of ions is given by following equation[12]

$$\Delta P_i = d\beta_s = \beta_s^\circ - \beta_s = \frac{Z_i^2 e^4}{2D^2 kT} \Sigma n_i Z_i^2 \qquad (1)$$

where β_s° and β_s are the compressibilities of solvent and solution respectively, k is the Boltzmann constant, D the dielectric constant of the medium, Z_i the valency, e the electronic charge, T the temperature and n_i the number of ions of ith kind per mole.

For any homogeneous non-dissipative fluid system, the velocity *(U)* of a compressional acoustic wave is related to the density *(ρ)* and isentropic compressibility *(β_s)*, by the equation.

$$U = (\rho\beta_s)^{1/2} \qquad (2)$$

Thus the variation of velocity with concentration in an electrolytic solution depends on the concentration derivatives of ρ and β_s as follows :

$$\frac{du}{dc} = \frac{-u}{2}\left(\frac{1}{p}\left\{\frac{dp}{dc}\right\} + \frac{1}{\beta_s}\left\{\frac{d\beta_s}{dc}\right\}\right) \qquad (3)$$

Equation (3) shows that the concentration dependence of the ultrasonic velocity is determined by the behavior of density and isentropic compressibility as the concentration changes. The quantity $d\beta_s/dc$ is always positive while $d\beta_s/dc$ has been found to be always negative for the ionic solutions. Since these factors have opposite signs, the velocity may either increase or decrease with concentration. In present work the velocity increases with in concentration of solutions similar to the solutions of thorium nitrate[6] (Tables 2, 3). The increase in the ultrasonic velocity can be represented by the equation

$$U = U^\circ + GC \qquad (4)$$

Where G is Guerasey constant.

Results and discussion

The velocities have been recorded in the Tables 2 and 3. It is obvious that the ultrasonic velocity increases with increase in concentration which can be expressed by the Eqs. 3 and 4. As it is evident from the data (Tables 2 & 3) , $[1/p \ (d\ p/dc\ )]$ and $[1/\beta_s\ (\ d\beta_s\ /\ dc)]$ are of opposite signs and the value of $[1/\beta_s\ (\ d\beta_s\ /\ dc)]$ is greater than $[1/p\ (d\ p/dc)]$ therefore the value of dU/dC is positive. The isentropic compressibility decreases with increase in concentration of calcium nitrate and ammonium nitrate (column 4 of Tables 1, 2) in each alcoholic solvents. This behavior is in agreement with the general trend observed in electrolytic solutions …. The lowering of compressibility of a solvent on dissolving an electrolyte in it is attributed to the influence of the electrostatic field of the ion on the surrounding molecules as reported by Ray and Prasad[10]. The isentropic compressibility of nitrates solutions is found to obey Bachem's relation $\beta = \beta_0 + AC + BC^{3/2}$, where A and B are constants whose values have been reported in Table 4.

Intermolecular free length is the predominant factor in determining the nature of ultrasonic velocity in the solution, which is the distance covered by a sound wave between the surfaces of the two molecules as given by the equation. $L_f = K\beta_s^{1/2}$, where K is the temperature dependent constant. Since the isentropic compressibility decreases with increase in concentration, Intermolecular free length also decreases in similar manner (Tables 2 & 3, column 5).The molar sound velocity *(R)* has been

Table 2 – Value of various parameter of Calcium nitrate in different alcoholic solution at 296.15K.

Concentration (Mole–1)	Density (g cm^{-3})	Ultrasound Velocity (ms^{-1})	Isentropic compressibility/ $\beta\times10^{12}$ (cm^2 $dyneS^{-1}$)	Inter molecular free length (A°)	Molar sound velocity C.G.S. unit	Specific acoustic impendance $Z\times10^{-4}$ (Rayl)	Solvation number n_s
Methanol							
0.010	0.7918	1134	98.22	0.6165	422.10	0.8978	9.02
0.020	0.7929	1135	97.90	0.6155	422.30	0.8999	8.53
0.030	0.7941	1136	97.57	0.6145	422.60	0.9022	8.46
0.040	0.7952	1137	97.29	0.6137	422.80	0.9040	8.08
0.050	0.7966	1138	96.96	0.6125	422.90	0.9063	8.12
0.060	0.7977	1139	96.63	0.6115	423.10	0.9088	8.15
0.070	0.7986	1140	96.36	0.6106	423.50	0.9103	7.96
0.080	0.7998	1141	96.05	0.6096	423.60	0.9124	7.91
0.090	0.8009	1142	95.72	0.6085	423.70	0.9147	7.99
0.100	0.8021	1143	95.42	0.6077	423.70	0.9168	7.89
Ethanol							
0.010	0.7900	1212	86.30	0.5779	622.70	0.9568	6.02
0.020	0.7914	1212	86.02	0.5769	622.90	0.9592	5.93
0.030	0.7928	1213	85.78	0.5761	622.70	0.9614	5.53
0.040	0.7942	1213	85.53	0.5753	622.90	0.9634	5.38
0.050	0.7953	1214	85.27	0.5744	622.70	0.9658	5.33
0.055	0.7960	1214	85.17	0.5741	622.90	0.9668	5.21
0.072	0.7980	1215	84.80	0.5728	623.20	0.9701	5.10
0.090	0.8000	1217	84.39	0.5715	623.60	0.9736	4.87
0.100	0.8014	1217	84.14	0.5707	623.70	0.9757	4.82
Isopropanol							
0.01	0.7862	1231	83.85	0.5696	820.60	0.9672	3.73
0.02	0.7875	1232	83.62	0.5689	820.40	0.9707	3.65
0.03	0.7885	1233	83.45	0.5682	820.80	0.9721	3.31
0.04	0.7897	1233	83.27	0.5676	820.40	0.9738	3.18
0.05	0.7910	1234	83.07	0.5669	820.20	0.9759	3.18
0.06	0.7922	1234	82.90	0.5663	820.20	0.9773	3.11
0.07	0.7933	1234	82.69	0.5657	820.00	0.9795	3.11
0.08	0.7945	1235	82.50	0.5650	820.20	0.9813	3.09
0.09	0.7955	1235	82.35	0.5645	820.00	09828	2.90
0.100	0.7966	1236	82.22	0.5640	820.20	0.9842	2.90

evaluated by using the equation $R = (M/p)(U)^{1/3}$, where M is the molar mass. It has been found that there is very slight variation in the values of molar sound velocity with increase in the concentration (Tables 2 & 3, column 6). Specific acoustic impedance *(Z)*, which is given by the product of ultrasonic velocity and density of the medium, shows increasing trend with increase in the concentration (Tables 2 & 3, column 7). A similar behavior has also been observed in the case of alcoholic solutions of thorium nitrate[6].

The fundamental aspect of interionic attraction theory has been found to be useful as the apparent molal properties, which are result of above theory, are mainly dependent on the concentration of the solutions. The apparent molal isentropic compressibility has been derived using the following equation

$$\phi_k = 1000/C\ p^\circ\ [p^\circ\ \beta_s - p\beta s^\circ] + m\beta_s^\circ/p^\circ \qquad (5)$$

where m is the Molecular weight of the solute.

The value of apparent molal isentropic compressibility (ϕ°_k) is obtained by extrapolation of value of ϕ_k, when it is plotted against square root molar concentration of solute according to following equation

$$\phi_k = \phi^\circ_k - S_k\ C^{1/2} \qquad (6)$$

Table 3 – Value of various parameter of Ammonium nitrate in different alcoholic solutions at 303.15K.

Concentration (Mole–1)	Density (g cm^{-3})	Ultrasound Velocity (ms^{-1})	Isentropic compressibility/ $\beta\times10^{12}$ (cm^2 $dyneS^{-1}$)	Inter molecular free length (A°)	Molar sound velocity C.G.S. unit	Specific acoustic impendance $Z\times10^{-4}$ (Rayl)	Solvation number n_s
Methanol							
0.01	0.7832	1122	101.42	0.6294	424.80	0.8788	5.87
0.02	0.7834	1123	101.22	0.6288	425.10	0.8798	5.25
0.03	0.7836	1124	101.01	0.6283	425.40	0.8808	5.22
0.04	0.7840	1125	100.78	0.6274	425.60	0.8820	5.31
0.05	0.7845	1126	100.54	0.6266	425.70	0.8833	5.37
0.06	0.7854	1126	100.42	0.6263	425.40	0.8844	4.97
0.07	0.7858	1127	100.19	0.6255	425.60	0.8856	5.06
0.08	0.7868	1128	99.89	0.6246	425.40	0.8875	5.31
0.09	0.7876	1128	99.79	0.6243	425.30	0.8884	4.99
0.10	0.7881	1129	99.55	0.6235	425.40	0.8898	5.08
Ethanol							
0.01	0.7820	1137	98.92	0.6276	614.20	0.8891	5.09
0.02	0.7832	1138	98.59	0.6265	613.70	0.8913	5.35
0.03	0.7836	1140	98.20	0.6252	614.00	0.8933	5.83
0.04	0.7846	1141	97.90	0.6243	613.70	0.8952	5.64
0.05	0.7855	1142	97.62	0.6234	613.50	0.8970	5.47
0.06	0.7860	1144	97.21	0.6221	613.70	0.8992	5.74
0.07	0.7871	1144	97.08	0.6217	613.30	0.9004	5.24
0.08	0.7876	1145	96.85	0.6209	613.20	0.9018	5.07
0.09	0.7882	1146	96.60	0.6201	613.10	0.9033	4.98
0.10	0.7888	1147	96.36	0.6194	613.00	0.9048	4.89
Isopropanol							
0.01	0.7740	1167	94.87	0.6146	816.40	0.9033	3.48
0.02	0.7745	1168	94.64	0.6139	816.30	0.9046	3.35
0.03	0.7753	1169	94.38	0.6130	815.90	0.9063	3.39
0.04	0.7760	1169	94.30	0.6128	815.40	0.9071	2.80
0.05	0.7770	1170	94.02	0.6118	814.70	0.9090	3.01
0.06	0.7775	1171	93.80	0.6111	814.70	0.9105	3.00
0.07	0.7781	1172	93.56	0.6103	814.50	0.9119	3.03
0.08	0.7788	1173	93.32	0.6095	814.20	0.9135	3.06
0.09	0.7791	1173	92.97	0.6084	814.50	0.9154	3.25
0.10	0.7798	1175	92.88	0.6081	814.00	0.9163	3.05

The value of ϕ_k vary linearly as the square root of the concentration for all six solutions in both systems the values of $\phi°_k$, are negative for all the solutions though its magnitudes are different (Table 4, column 6). The slope (S_K) as obtained from Eq. (6) is positive in all the three solvents for both systems similar to the findings of Rajagopal and Gladson[11]. The value of S_K depend on the dielectric constant of the medium. Since low dielectric constant enhances electrostatic attraction, it appears reasonable to infer the positive slope is due to this effect. The isentropic compressibility data have also been used to measure the solvation number of salts. The assumption has been made here that the ions as well as the solvent molecules in immediate contact with ions are incompressible. This is because the ions add some electrostatic stiffening on the adjacent solvent molecules, which is considered to be equivalent to a large internal pressure on these solvent molecules. The expression giving the solvation number (n_s) is

$$Lim_{c \to 0}\, \phi_k, = \frac{(Vf - n_1 V_1°)\beta°_s}{n_2} \quad (7)$$

$$= n_s V°_1\, \beta°_s \quad (8)$$

Table 4 – Value sof various parameters of Calcium nitrare and Ammonium nitrate in different alcoholic solutions.

Solvent	A	B	G	S_k	$\phi_k°$	Solvation number n_s
Calcium nitrate						
Methanol	–36.75	18.75	90.0	25.00	–33.00	8.27
Ethanol	–31.00	20.00	54.0	27.77	–29.25	5.83
Isopropanol	–24.25	17.05	48.0	25.00	–21.50	3.34
Ammonium nitrate						
Methanol	–23.5	8.33	98.0	15.00	–19.8	4.8
Ethanol	–40.0	38.25	113.0	33.33	–39.5	6.8
Isopropanol	–27.0	15.00	85.0	10.12	–24.5	3.3

where n_1 is the number of moles of solvent and n_2 is the number of moles of solute; V_f is the volume of free solvent and $V°_1$ is the molar volume of the solvent. The solvation numbers obtained by using Eq. (9) are given in Tables 2 & 3.

Values of ns have also been calculated from Passynsky's relation.

$$n_s = \frac{n_1}{n_2}\left(1 - \frac{V\beta_s}{n_1 V_1° \beta°_s}\right) \quad (9)$$

where V is the volume of the solution containing n_2 moles of solute and $V°_1$ is the volume of solvent. The solvation numbers obtained using above expression are given in Table 4. Values obtained using Eqs (8) and (9) are quite close to each other.

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Optimization of process parameters to develop nanoemulsion by ultrasound cavitation

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Nanoemulsions are colloidal dispersions of oil and water stabilized by interfacial layer of surfactant with droplet size ranging between 20 nm and 200 nm. The reduced droplet size makes the system optically transparent/translucent due to weak scattering of light waves. Also the very low droplet size of the nanoemulsion improves the stability of the system when compared to emulsion with greater droplet size. In the present study, plant essential oil based oil-in-water nanoemulsion was formulated by ultrasound cavitation method which was stabilized by interfacial layer of non-ionic surfactant. Development of oil-in-water nanoemulsion was optimized for different process parameters such as surfactant type, surfactant concentration and emulsification times to obtain nanoemulsion with lower droplet size and greater stability.

Keywords: Ultrasound cavitation, Nanoemulsion, Plant essential oil, Tween 20, Tween 80.

Introduction

Nanoemulsions are dispersions of oil and water stabilized by surfactant and/or co-surfactant with droplet size in the range of 10-100 nm [1]. Nanoemulsions serve as attractive delivery systems for lipophilic bioactive ingredients such as drug in pharmaceutical industry; for flavors and antimicrobial agents in the food industry; for skincare products in cosmetics industry [2-3]. The applications of nanoemulsion owes to their advantages over conventional emulsions like high stability and low turbidity which makes them attractive delivery systems.

Ultrasound irradiation is a high energy method to prepare nanometric-range emulsion droplets. Emulsion formulation by ultrasound cavitation was patented in 1944 in Switzerland. It is one of the efficient techniques for formulating nanoemulsion with low polydispersity index and greater stability [4]. Ultrasonic emulsification exploits very high frequency sound waves with 20 kHz for developing acoustic cavitations. These cavities collapse and produce intense heating of ~5000°C, high pressure about 1000 atm and high rate of heating-cooling above 1010 K/s [5-6] which reduces emulsion droplet size [7]. The objective of the present study is to optimize process parameters to formulate stable nanoemulsion with small droplet diameter using ultrasound cavitation method.

Materials and Methods

Chemical reagents

Basil oil, Cinnamon oil, Tween 20 and Tween 80 were purchased from Sigma Aldrich, India. Sesame oil and mustard oil were obtained from local super market, Vellore, Tamil Nadu. Double distilled water was used for all the experiments.

Nanoemulsion preparation

Nanoemulsion was prepared by ultrasound cavitation method using different plant essential oil, non-ionic surfactant (Tween 20 or Tween 80) and water. Nanoemulsion was formulated in two steps; first, coarse emulsion was prepared by mixing oil, surfactant and water. Second, the coarse emulsion was subjected to ultrasound cavitation using a Sonicator (Frequency: 20 kHz, Maximum power output: 750 W). Nanoemulsion formulation process was optimized for different parameters to reduce droplet size and enhance stability:

1. *Oil type :* Nanoemulsion was formulated using crude (viscous) oil and refined (less viscous) oils

to check the effect of oil type and oil viscosity on the droplet size of nanoemulsion.

2. *Surfactant type :* Surfactants stabilize the emulsion system by lowering the interfacial tension at oil/water interface. Hydrophile-lipophile balance (HLB) value of the surfactants play important role in determining the type of emulsion. High HLB value surfactants aid in formulating oil-in-water nanoemulsion, whereas low HLB value of surfactants formulate water-in-oil surfactants. Geometry of surfactants also play crucial role in determining emulsion droplet size.
3. *Surfactant concentration :* Impact of surfactant concentration on the emulsion droplet size was studied by varying the surfactant concentration.
4. *Sonication time :*

Impact of sonication time was studied by subjecting the coarse emulsion to ultrasound cavitation for different sonication time. In regular interval of ultrasound cavitation process, samples were collected and nanoemulsion droplet size was determined.

Nanoemulsion optical property

Turbidity of all the formulated nanoemulsions was visually determined and graded as transparent/translucent/turbid.

Nanoemulsion droplet size

Droplet size of all the nanoemulsion formulations were determined using a particle size analyzer (Brookhaven Instruments Corporation, USA) by dynamic light scattering (DLS) technique.

Nanoemulsion droplet morphology

Morphology of mustard oil emulsion was visualized by transmission electron microscopy (TEM). Selected nanoemulsion was negatively stained with phosphotungstic acid and one drop of was placed on copper grid. Electron micrograph was obtained by using a transmission electron microscope (Tecnai10, Philips).

Results and Discussion

Impact of sonication on optical property of nanoemulsion

Optical property is considered to be one of the important parameters while developing delivery system for food and beverage products. Emulsion was formulated using basil oil, cinnamon oil, mustard oil and sesame oil. Coarse emulsion (before sonication) was turbid in color but after sonication the emulsion changed to optically transparent. This decrease in turbidity can be explained by reduced droplet size after sonication which results in weak scattering of light and making the formulated nanoemulsion system optically transparent.

Impact of oil type on nanoemulsion droplet size

Nanoemulsion was formulated using viscous oil (mustard oil and sesame oil) and flavored oil (basil oil and cinnamon oil) by ultrasound cavitation. Droplet size of basil oil, cinnamon oil, sesame oil and mustard oil emulsion were 30 nm, 62 nm, 175 nm and 240 nm respectively after 15 min of sonication time (Fig. 1).

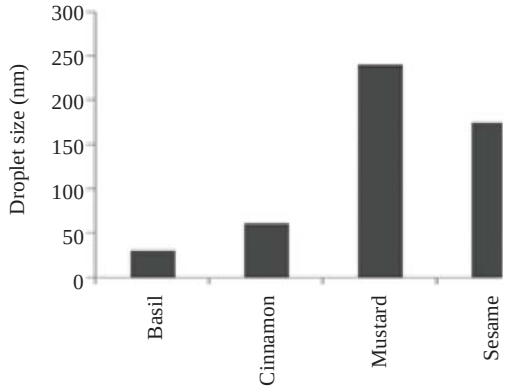

Fig. 1 Effect of oil type on nanoemulsion droplet size.

Effect of oil type on emulsion droplet size may be due to viscosity of the oil. Our results corroborated with earlier reportsthat different oil system form emulsion with different droplet size i.e. flavor oils form emulsion with reduced droplet size when compared to triglyceride oils [1,8]. Kolb et al (2001) also have shown that increase in the viscosity of the oil system increases emulsion droplet size [9].

Impact of surfactant type on nanoemulsion drop size

The HLB value is commonly used to select surfactants for stabilizing emulsions. In the present study, low molecular weight non-ionic surfactants such as Tween 20 and Tween 80 were used to formulate nanoemulsion for their high HLB value and low molecular weight. Basil oil nanoemulsion (sonication time = 15min) with droplet size of 30 nm was obtained with Tween 80 whereas droplet size was found to be 45 nm in case of Tween 20 (Fig. 2).

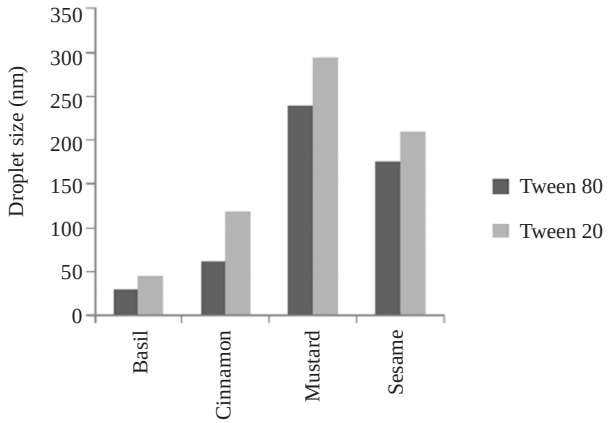

Fig. 2 Effect of surfactant type on nanoemulsion droplet size

Non-ionic surfactants stabilize emulsions by stearic stabilization which involves the repulsion between the bulky molecular groups. Tween 80 is more effective in minimizing emulsion droplet size when compared with Tween20. This is due to the fact that presence of double bonds in the non-polar chains of Tween 80 favors the formation of nanoemulsion with minimized droplet diameter.

Impact of surfactant concentration on nanoemulsion droplet size

Surfactant concentration exhibited an indirect relation with nanoemulsion droplet size. Fig. 3 shows droplet size of nanoemulsion using different concentration of Tween 80.

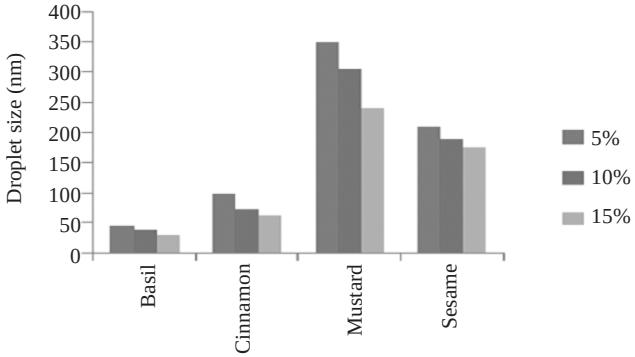

Fig. 3 Effect of surfactant concentration on nanoemulsion droplet size

This goes along with our previous study that droplet size of nanoemulsion gets minimized with increase in surfactant concentration [10-15].

Impact of sonication time on nanoemulsion droplet size

Emulsification time exhibited negative correlation with droplet size (Fig. 4). Effect of emulsification on droplet size was studied using Tween80 as surfactant. With increase in sonication time from 5 min to 10 min and 15 min, droplet size reduced.

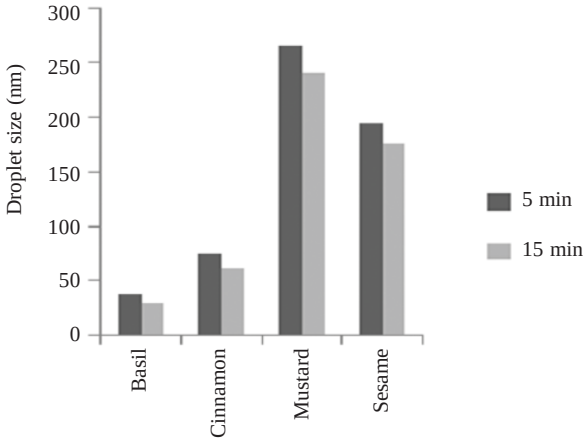

Fig. 4 Effect of sonication time on nanoemulsion droplet size

Nanoemulsion droplet morphology

Morphology of basil oil nanoemulsion was visualized by transmission electron microscopy (TEM) (Fig. 5). The nanoemulsion droplets were spherical in morphology and droplet size was in the range of 20-50 nm. TEM analysis also provided data on droplet size of nanoemulsion *i.e.* the droplet size range obtained by TEM analysis corroborated with the data obtained using particle size analyzer.

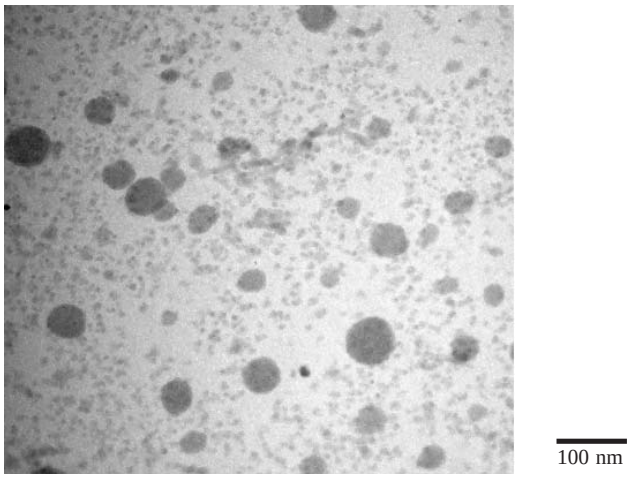

Fig. 5 Transmission electron micrograph of basil oil nanoemulsion

Conclusion

A stable nanoemulsion with droplet size 30 nm was formulated using basil oil and non-ionic surfactant Tween80 by ultrasonic emulsification. In the present study it is observed that oil type, surfactant type, surfactant concentration, mixing ratio of oil-surfactant and sonication time showed significant influence on droplet size of nanoemulsion. Tween80 was comparatively more effective than Tween20. Droplet size decreased with increase in emulsification time and surfactant concentration, whereas the reverse trend was observed in turbidity.

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Inspection on aluminum plates by implementation of NDT techniques

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Aluminum alloys consist of different grade namely HE-15, 30, and 20 respectively. These alloys are selected from 6XXX series of aluminum group. All the alloys are fabricated from machining into rectangle shape in the form of 150mm in length, 120mm in width and 12mm in thickness. The main concept arises during the interpretation of alloys is defects are notified. The defects are traced out from the aluminum alloys by NDT methods, ultrasonic method and liquid penetrant method. These NDT techniques are conducted on the all aluminum alloys according to ASNT procedure to trace out defects in the materials. After, pulse-echo method of A-scans and experimented on the aluminum alloys, On the other hand water soluble dye penetrant test also performed to trace out the surface defects. Lastly, various orientations of defects are mapped out through the implementation of NDT methods and remedy behind the defects are traced out due to improper handling of welding process

Keywords: Aluminum alloys, NDT methods, Pulse-echo technique, Liquid penetrant method, A-scan

Introduction

NDT is the use of special equipment and methods to learn something about an object without damaging the object. The term nondestructive testing usually implies that a nonliving object, such as a piece of metal, is being evaluated.NDT methods are used to make sure that the important parts on aeroplanes and automobiles and in nuclear power plants are free of defects that could lead to an accident. NDT is also used in many other industries to make sure that parts do not have defects that would make the customer unhappy. The inspection and measurement methods used in the field of NDT are largely based on the scientific principles of physics and chemistry.

Non-destructive testing (NDT) is a wide group of analysis techniques used in science and industry to evaluate the properties of a material, component or system without causing damage. The terms nondestructive examination (NDE), nondestructive inspection (NDI), and nondestructive evaluation (NDE) are also commonly used to describe this technology[1]. As NDT does not permanently alter the article being inspected, it is a highly valuable technique that can save both money and time in product evaluation, troubleshooting, and research. Common NDT methods include ultrasonic, magnetic-particle, liquid penetrant, radiographic, remote visual inspection (RVI), eddy-current testing, and low coherence interferometer.

Aerospace materials

Aluminum Alloy HE-15 (2014) : Aluminum Alloy HE-15 (2014) is a copper based alloy with very high strength together with excellent machining characteristics. Alloy 2014 is commonly used in many aerospace structural applications due to its high strength.

Aluminum Alloy HE20 (6061) : Aluminum 6061 is an extremely versatile heat treatable aluminum alloy. 6061 has a wide range of mechanical and corrosion resistance properties as well as having most of the good qualities.

Aluminum Alloy HE30 (6082) : Aluminum alloy 6082 is a medium strength alloy with excellent corrosion resistance. It has the highest strength of the 6000 series alloys. Alloy 6082 is known as a structural alloy. In plate form, 6082 is the alloy most commonly used for machining.

Welding technique

TIG welding is implemented to aluminum alloys (HE-

15, HE-20, HE -30) with respective weldability of alloys. For the best appearance, highest quality and leak free welds on aluminum, AC TIG (Alternate current, tungsten inert gas) welding is the process of choice. The primary gas used is argon and in some applications on thick aluminum when additional penetration is needed an argon/helium mixture or pure helium is used. TIG welding offers the user the greatest amount of flexibility to weld the widest range of material and thickness[2]. AC TIG welding is also the cleanest weld with no sparks or spatter.

Sample Preparation

Chemical composition

Aluminum alloys have either been developed for, or have come to prominence through, their use for aerospace purposes. These uses often require exceptional performance, strength or heat resistance. The chemical composition of aluminum alloys is chosen for conducting NDT methods are shown below :

Table 1 –Chemical Composition of HE-15

Element	HE-15	HE-20	HE-30
Copper	3.8-5.0	0.15-0.40	0-0.1
Magnesium	0.2-0.8	0.8-1.2	0.6-1.2
Silicon	0.5-1.2	0.7 max	0.7-1.3
Iron	0.7	0.4-0.8	0-0.5
Manganese	0.3-1.2	-----	0.4-1.0
Zinc	-----	0.25 max	0-0.2
Titanium	-----	0.15 max	0-0.1
Cromium	-----	0.04-0.35	0-0.25
Aluminium	Balance	Balance	Balance
others	1.5	0.05 max	0.15

Workshop Method

Different types of aluminum alloys (HE-15, HE-20, HE -30) were fabricated and machined from the respective task in the form of rectangular shape. Dimensions of the sample were similar for all aluminum alloys such as, thickness 12 mm, length 150 mm, and breadth 120 mm. These plates were machined by SAMRAT model 390 lathe machines for experimental inspection of defects produced by conducting TIG welding technique.

Welding task

The types of welding carried out for all aluminum alloys was TIG and V butt joint was prepared by machining[3]. Welding parameters maintained for aluminum alloys for good weldability are as shown in Table 1.

Table 1 –Welding Parameters

Current	Gas flow	Electrode	Filler metal	Welding speed
200- 220 amps	10m/s	Tungsten	Aluminium 2014	10cm /min

Fig. 1 V-Groove

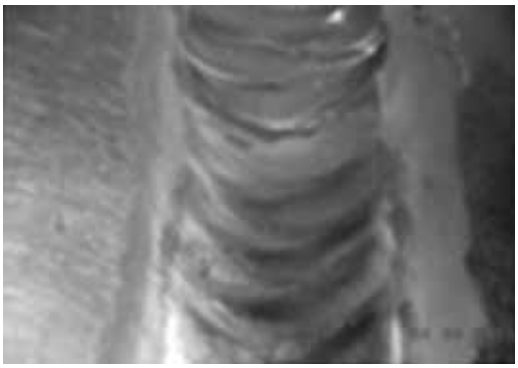

Fig. 2 TIG welding

Experimental Study

Two types NDT methods were implemented on the aluminum alloys specifically pulse-echo ultrasonic method and liquid penetrant method. Ultrasonic method gives out deeply involved flaws internal of the alloys, on the other hand liquid penetrant method is used for surface defects only.

Ultrasonic method

In ultrasonic testing, an ultrasound transducer connected to a diagnostic machine is passed over the object being inspected. The transducer is typically separated from the test object by a couplant (such as oil)[4]. Internal defects are notifed in alloys by way of graphical representation of defects as given below.

1. Acoustic signals from the same reflecting surface will have different amplitudes at different distance from the transducer.
2. DAC provides a means of establishing a graphical reference level sensitivity as a function of sweep distance on the A- scan display. Results of internal defect trace out are in the given Fig. 3.
3. A-Scan echoes are displayed at their non-electronically compensated height and the peak amplitude of each signal is marked on the flaw detector screen or, preferably, on a transparent plastic sheet attached to the screen[5].

Inspection on HE-15 alloy

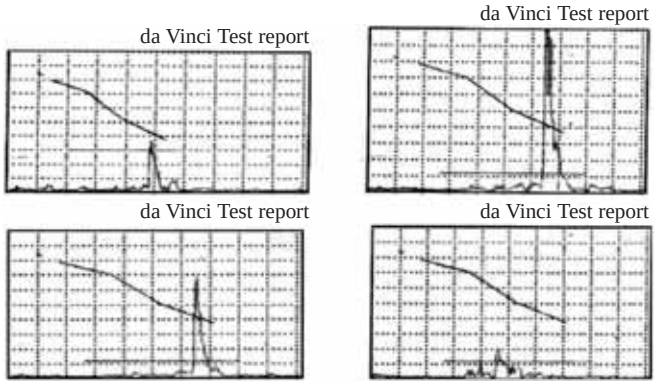

Fig. 3 Graphical representatin of defects in Aluminum HE-15.

.Inspection on HE-15 alloy

Inspection on HE-20 alloy

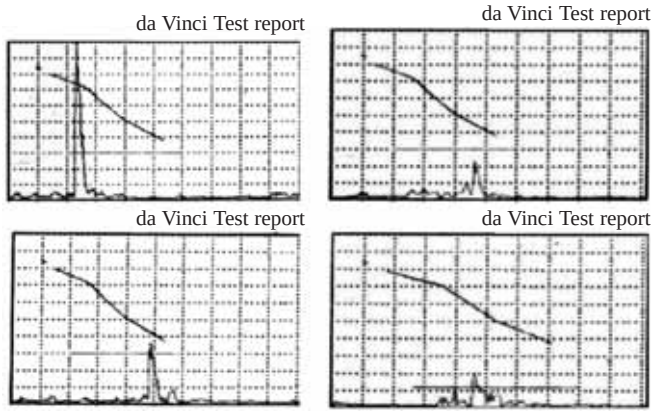

Fig. 5 Graphical representatin of defects in Aluminum HE-20

Liquid Penetrant Testing

In this testing we get only surface defects which are open to surface. So we got three defects in SS materials and three defects in aluminum samples.

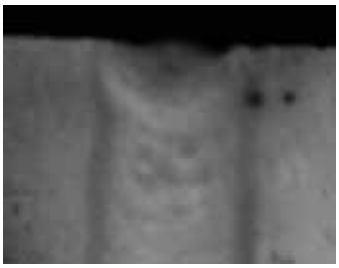

Fig. 6 Pin hole in Aluminum HE-15

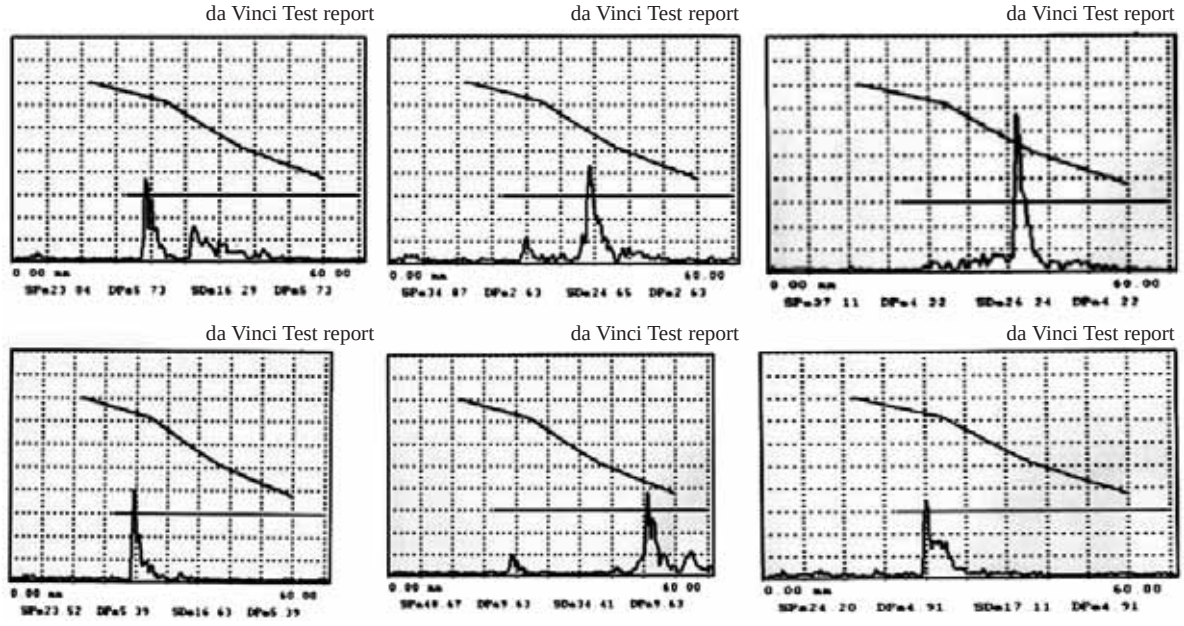

Fig. 4 Graphical representatin of defects in Aluminum HE-30

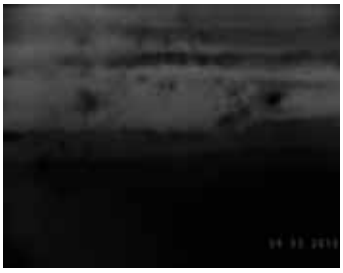

Fig. 7 Blow hole in HE-20

Fig. 8 Pin holes on weld region HE-30

Fluorescent penetrant testing

- Fluorescent penetrant inspection is done from procurement industry services. Fluorescent dye is applied to the surface of a non-porous material in order to detect defects that may compromise the integrity or quality of the part in question.
- Fluorescent penetrant method is followed according to "ASTM E 1417 "Standard practice for liquid penetrant examination.
- During inspection of all samples no defects are traced out in the materials. Fluorescent penetrant method reports the sensitivity of defects which are open to surface only[6-9].

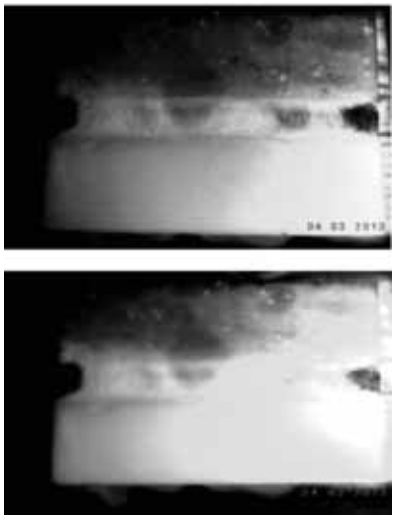

Fig. 9 Spatter on surface of Aluminum HE-20

Ultrasonic Phased Array Test Results

The abilities of phased array ultrasound to detect discontinuities in weld sample. The embedded discontinuity inclusions and porosity of two samples of HE 15 materials were tested[8]. Blow holes, porosity were observed at the welded region. In this test the accurate size of blow holes were 2mm to 3mm and porosity less than 1mm as shown in Fig. 10.

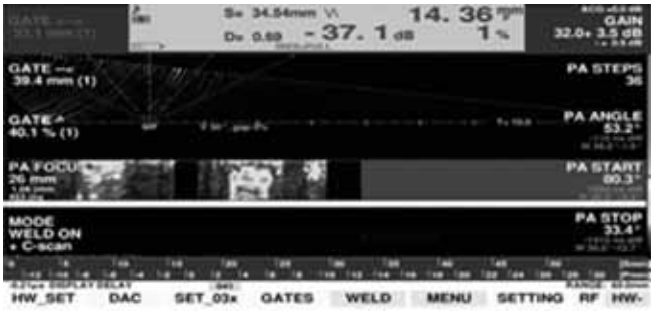

Fig. 10(a) Defect at 14.36 mm

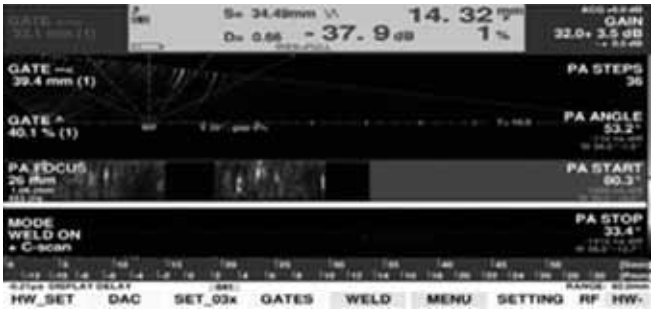

Fig. 10(b) Defect at 14.3 mm

Results and Discussion

- Two internal discontinuities were detected through Ultrasonic Testing, discontinuities are showed in Figs. 7-8.
- No surface and sub-surface defects were detected through Magnetic particle testing
- No Surface discontinuities were detected through Liquid Penetrant testing.

Acknowledgements

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Forthcoming Conferences

1. The 2nd Conference on New Advances in Acoustics (NAA 2016); Beijing, China, February 28 to March 1, 2016; http://www.engii.org/conf/NAA/2016Feb/
2. 2015 IEEE International Ultrasonics Symposium (IUS) 21 Oct - 24 Oct 2015, Taipei International Convention Center (TICC); Taipei, Taiwan; ewh.ieee.org/conf/ius/ius_2015/
3. ICU 2016: 18th International Conference on Ultrasonics: Conference Code: 16US03ICU; Conference Dates March 1-2, 2016; Holiday Inn Miami Beach, 4333 Collins Ave Miami Beach, FL 33140, USA; https://www.waset.org/conference/2016/03/miami/ICU
4. International Conference on Condensed Matter & Applied Physics; Veterinary Auditorium, Bikaner (India), October 30-31, 2015. http://www.iccindia15.com/index.php
5. NANOS2015, GITAM University, Rushikonda, Visakhapatnam, 530045, Andhra Pradesh, India; December, 14th to 17th, 2015; nanos2015.gitam.edu/
6. 2nd International Conference and Expo on Smart Materials & Structures February 29-March 02, 2016 Philadelphia, USA - See more at: http://smartmaterials-structures.conferenceseries.com/#sthash.kJPMNC4V.dpuf,
7. International Conference on Engineering Physics, Ultrasonics and Materials at THE NORTHCAP University, Gurgaon, June 3-4, 2016.

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