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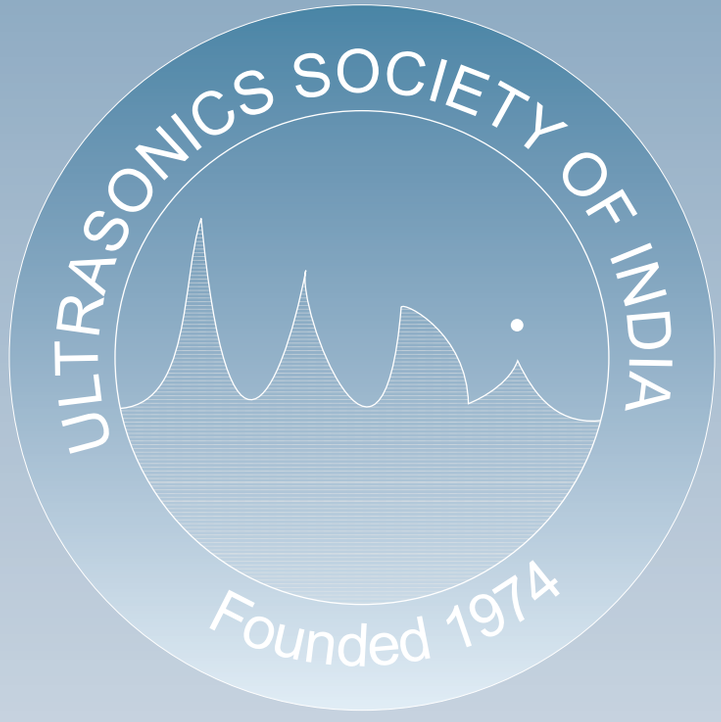

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EDITORIAL

Dear Colleagues,

I am pleased to inform you that Journal of Pure and Applied Ultrasonics has received recognition from UGC for inclusion in the UGC-CARE list of the journals published from India. Further, JPAU has found a place in Indian Citation Index (ICI). Both of these status for JPAU should act as additional incentive to contributors of papers to publish their research papers and review articles in JPAU in greater numbers.

The executive Council of Ultrasonics Society of India (USI) has decided to review and update the academic particulars of the members in USI handbook regularly at intervals of approximately three to six months and upload the same on USI website. I am pleased to inform you that the handbook updated December 2021 has been uploaded on the website.

In this issue a review article by Dr V R Singh has been published on medical applications of nano-ultrasonic sensors and IOT systems. The article also summarizes some of his own research carried out by Dr V R Singh and his research students during the course of his scientific work in this field at NPL References include a large number of research papers published in this field. I hope the readers would find this work useful.

K. Balasubramaniam group from Nondestructive Evaluation Center (NDE), I.I.T. Madras have published in this issue an innovative work on properties of phononic crystal acoustic lens from periodic and aperiodic structures.

Some more innovative technologies have been developed in recent years. These include a temperature sensor for mapping temperature in high temperature furnaces, ovens, etc. and an improved ultrasonic beamformer for higher resolution imaging organs in human body developed at NDE centre at I.I.T., Madras. Another development worth a special mention is a 100 μm transducer using MEMS for use in arrays for imaging applications developed at I.I.Sc., Bangalore. Such work could inspire our readers to take up further research in this area.

Announcement for Dr T K Saksena award would soon be made in September 2022. Ph.D. students who have obtained their Ph.D. degree in last two years would be eligible to apply.

Recent Ph.D. awardees from ultrasonics discipline are invited to publish review papers on their thesis work in JPAU. Besides this, they are encouraged to submit one-page summaries of their Ph.D. thesis for publication in JPAU.

Further, authors may consider publishing research papers on their work in JPAU which were presented and published in proceedings of conferences, symposia, seminars, etc. Authors may like to make changes in manuscripts of such papers based on feedback obtained in the presentations made at the respective event and submit the same to JPAU for consideration of their publication.

In addition to the papers in the area of ultrasonics the journal also considers publication of papers related to piezoelectric devices and materials. Researchers are invited to send for publication of their papers on ferro-electric (piezoelectric), magneto-striction and other electrostriction devices and materials.

— S. K. Jain
Chief Editor
Journal of Pure and Applied Ultrasonics

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Nano-ultrasonic sensors and IOT systems for health care applications

V.R. Singh[1*] , P. Rajagopal, K. Balasubramaniam and Kanika Singh[2]

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With the development of science, ultrasonic technology is finding its newer and newer, applications in different fields in the measurement of the physical parameters very precisely at faster speed. The size of the transducer devices has become of nano-size and measurement has enabled to nano-measurement. In the present paper, recent developments in nano-ultrasonic sensors and IOT (Internet of Things) based systems are described for different health care applications. AI (Artificial Intelligence) in ultrasonic measurements and use of block chain systems are also discussed for specific applications. Design and development of nano-ultrasonic devices and IOT based systems are explained here.Case studies of cancer research and hyperthermia for treatment of deep-seated tumours in the brain are given. The study is very useful in the clinical diagnosis and treatment of abnormalities/diseases in the human beings quickly at low cost.

Keywords: Nano-ultrasonic sensors, IOT (Internet-of-Things) systems, healthcare, blockchain technology, cancer research, AI (Artificial Intelligence), hyperthermia, brain tumours.

Introduction

Ultrasound as an Effective Measurement Tool. However, more sophisticated sensor systems are still required to be developed for fast measurements in an intelligent manner[1-106].

Ultrasound is an effective tool for the measurements in every branch of science, technology and medicine. The technology has progressed to nano-sensors and IOT (Internet-of-Things) based systems for quick and reliable measurements. Mainly, different types of sensors and systems developed at the Laboratory are (i) piezo-resistive/semiconductor type, (ii) piezoelectric/ultrasonic type, (iii) piezo-composite type, (iv) biochip based, (v) point-of care type and (vi) ubiquitous health care type[4-11].

Ultrasonic Nano-Sensors : The design and development of nano-ultrasonic transducers and sensors are used for good biological and industrial applications. Nano metric wavelengths are generated in acoustic waves depending on mechanical resonators, prepared after finite element modelling allowing the tuning of the design parameters for optimum performance. These are fabricated as nano-scale devices.

Nano-composite materials are used in nano-size form with different composites as a combination of piezo-electric material and composites like polymers. These are made by using top-down approach where plate structures are built up and patterned by using photolithographic technique to get the device.

Earlier Nano-Ultrasonic Sensors : The historical research in nano-ultrasonic sensors, devices and systems is given[1-106] as follows:

Nano-biomedical Sensors : Recent developments in biomedical sensors are cited well in the literature by A. Mehmet Engin *et al.* and in other publications[24-26].

Piezoelectric Micromachined Ultrasound Transducer (PMUT) Arrays for Integrated Sensing, Actuation and Imaging' have been described by Y. Oiu *et al.* Further, it has given low power transducers and transducer arrays integrated with electronic systems. Generally, piezo electric micro-machined ultrasound transducers which are diaphragm-like thin film flexural transducers are formed on silicon substrates as integrated transducer arrays. Microfabrication technique is used to develop such devices with electrical interconnection and integration on-chip electronics, with

tuneable frequency. Design and fabrication of nanoscale ultrasonic transducers: have been discussed by Richard Smith *et al.* in detail[30-46].

Tissue Phantom for Calibration of UltrasonicSensors has been discussed by S. Yadav et al.: Tissue phantoms are, generally, used in the calibration of therapeutic and diagnostic systems. Thus, Tissue-Mimicking (TM) phantoms have been developed and studied here for various ultrasonic output parameters. These phantoms have been developed by using agar-based Tissue-Mimicking Materials (TMM) with alumina as an absorption material. A pulser - receiver (make Panametrics, Model-5800, Waltham, MA 02154, USA) has been used to measure ultrasonic velocity and attenuation coefficient, which were found to be 1540-1550 m/s and attenuation 10.0-35.0 dB/m-MHz at frequencies from 2.5 MHz to 5.0 MHz. These ultrasound test phantoms incorporating TM material are useful in the performance evaluation of medical ultrasound systems.

An overview of biomedical sensors is given as the key component in various medical diagnostic instruments, detection sensors, drug analysis and screening sensors, and micro-nano-systems, for ultra-ultrasound to revolutionise technology given in Nano Magazine, https://nano-magazine.com › news and by Sanjay Yadav, *et al.*

Precision Ultrasonics : Warwick Bowen has discussed precisionsensing Initiative and the calibration as well as high resolution of biomedical imaging to detect properties to study the structure of biological.tissues. Precision ultrasound sensing on a chip has also been studied by S. Basiri-Esfahani, 2019. With the wide adoption of ultrasound methods in biomedical and centimetre-scale sensors, the limit drops to tens of nano-pascal levels, as cited.

Health Care Applications of Nano-Ultrasonic Sensors

Some of the healthcare applications of nano-ultrasonic sensor systems[26-37] are described as follows:

(i) **A novel ultrasound technique for detection of osteochondral defects in the ankle joint:** A Parametric and Feasibility Study. Osteo-chondral defects (OCDs) in the ankle are diagnosed with ultrasound non-invasively, on wave propagation through the ankle joint. OCDs are differentiated withsignal deviations from a reference signal associated with the healthy joint.

(ii) **Ultrasonic contactless sensor for breathing monitoringis given by Phillippe *et al.* :** Human breathing during a long period is used to detect sleep disorders like apnoea, where the person stops breathing for several periods during sleep. In polysomnography, the standard for sleep disordered breathing analysis, chest movement and airflow are studied to monitor the respiratory activity, and an ultrasonic device quantifies the breathing activity, without contact and without any perception the subject. The device measures the frequency shift produced by the velocity difference between the exhaled air flow and the ambient environment, *i.e.*, the Doppler effect, to use signal processingto separate the effects of breath from those due to subject movements from the Doppler signal.

(iii) **Ultrasonic Systems for Biomedical Sensing :** A review is given about ultrasonic sensor systems for biomedical sensing by Prof. Dr. Jae Youn Hwang, in Proceedings of 22nd Int. Congress on Acoustics.

The ultrasound and its relevant multimodal system have been widely utilized as a promising technology in biology and medicine. Currently, ultrasound sensing and imaging systems have become one of the key methods for measuring cell and tissue properties, such as molecular, mechanical, and chemical properties. The studies are given on on new ultrasound imaging and sensing systems, ultrasound-based multimodal systems, mobile ultrasound systems, ultrasound transducers, and their applications in medicine and biology.

(iv) **A digital multigate doppler method for high frequency ultrasoundby Paul C. Lauterbur. *et al.* :** High frequency ultrasound Doppler technique is used to assess the morphology and hemo-dynamics of the microcirculation of the blood, to get output in B-mode.Tissues are diagnosed with ultrasound non-invasively, on wave propagation through the ankle joint. OCDs are differentiated with signal deviations from a reference signal associated with the healthy joint.

Materials and Methods

Design. fabrication and development aspects of different types of materials and sensors[5-48] are given as follows:

Sensors from biological tissues : Some samples of lymphoid tissues of mesenteric mass were collected from different hospitals like King George Medical University, Lucknow, India from patients of age 35 to 45 years. These samples were preserved in 10% formalin solution. Their parallel sections were made with scalpel. They all were hard and firm masses, cut with gritty sensation. In appearance these were pinkish-white and glistening on cut.

For calibration of instrument, standard samples of Perspex were used and results of ultrasonic parameters were obtained by double-probe through transmission technique. Sample was kept between two matched ultrasonic transducers as transmitter and receiver of same frequency (3.5 MHz) made at NPL, New Delhi, India by using discs (10 mm in diameter of PZT-5 (lead zirconium titanate) material An ultrasonic pulser-receiver (Panametrics model 5052 PR) was used to excite the transmitting transducer. The pulses after passing through sample were received by another matched transducer and displayed on cathode ray oscilloscope (OS 300C-20MHz, L&T Gould make). Ultrasonic velocity and other parameters were then determined

Nano-composite based sensors : Piezo/ceramic and polymers were used to develop nano-composite material (see Fig. 1 for conductance results).

Biochip-based sensors : A biochip is a collection of miniaturized test sites (microarrays) arranged on a solid substrate that permits many tests to be performed at the same time in order to achieve higher throughput and speed.

Bone Sensors : Development of new smart biomedical sensors has been made with the bone as piezoelectric in nature, biological bone material is used to fabricate transducer devices and sensors to be used as orthopaedic devices. This would also assist directly in the evaluation of bone conditioning and hence in the detection of bone abnormality like bone fracture. The smart systems thus help in recommending better devices and implants, when needed. Electro-magnetic and Hall's effect in bone are studied to prove that such effect assists in early healing of bone fractures as well as osteoporosis problem of patients. This resent sensor technology would be a boon to orthopaedic and rehabilitation engineering.

New piezoelectric sensors with gall bladder stone material : Gall bladder stone, *in vitro*, were characterised and piezoelectric sensors were made by following the process of bone sensor development process.

Nano-cancerdiagnosis : New nano-biotechnological devices have been developed to solve problems with the conventional systems. In cancer research, there are three key areas where researchers expect nano to fight cancer. First, diagnosis is to be improved with delicate sensors. Vibrating nano-cantilevers that change frequency when they bind to tumour cells may yield ultra-early lab tests for the disease. Second, drug delivery systems using tiny particles are to carry drugs through the bloodstream to tumours. Specially designed "stealth" particles may sneak past the immune system, allowing more of the drug to accumulate in the tumour. Finally, medical imaging is also to be improved: For instance, iron-bearing nanoparticles that preferentially accumulate in tumours may make them show up earlier in MRIs. Different types of nano-sensors, carbon nanotubes, polymer-based devices and biochips, etc have emerged which are sensitive and responsive enough for cancer detection. New smart nano-sensors, lab-on-chip systems and new nano-materials used for the diagnosis of cancer have been developed.

Cancer Nanotechnology : Cancer is a serious disease, as known worldwide. Cancer nanotechnology has been studied by using nano-ultrasonic sensor systems to find diagnostic and treatment of diseases with ultrasonic characterisation. Other techniques are use of biochips, biosensors and biologically inspired devices.

The lab-on-chip devices : The lab.on. chips have several distinct advantages over the current cell culturing and detection methods, which include ease of use for cell culture and reaction, rapid hybridization and sensitive detection. A nano-scale tool that distinguishes soft cancerous cells from stiffer normal ones can save lives by making it easier to diagnosis cancer. Using atomic force microscopes, the surface of living cancer cells is found to be 70 per cent 'softer' than the healthy counterparts, in the elasticity of lung, reast and pancreatic cancers, to provide a powerful means of detecting malignant cells. Anatomical pieces of breast, bone and other tumours have been studied for ultrasonic and other physical parameters, to determine design parameters of cancer instrumentation. The samples of the breast tumours, in vitro, have been studied in the laboratory.

The samples were shaped to have parallel faces for ultrasonic measurements.

U-Health care and POC devices : Different types of sensors and biochips have been developed for both diagnostic and therapeutic applications. Development of piezo-resistive semiconductor type, piezoelectric ceramic type, piezo-composite-based and biochip-based devices has been made. New ultrasonic and other sensors also have been developed with new piezo-composite materials for ubiquitous health care applications. The development of ubiquitous healthcare systems is used with different healthcare applications. Nano- PZT (Lead Zirconium Titanate), quartz and other such piezoelectric materials have been utilized for the development of nano-ultrasonic sensors with improved resolution, better sensitivity, directivity, and stability, *etc*. The ultrasonic sensors become important part of sensor networking in U-health care systems also.

New piezo-composite-based sensors have been developed for biotelemetry and other ubiquitous healthcare applications. The piezo-composite sensor material is developed by combining a piezoelectric ceramic and a passive polymer to develop transducers with enhanced electromechanical coupling and better acoustic impedance close to that of the tissue. Thus, medical ultrasonic imaging sensors with high sensitivity and good focusing can easily be developed for smart u-healthcare systems and point of care systems.

U-health care technologies are based on e-health, biomedical sensors and networking, with super highways, internet and RF-ID technology, *etc.* which are developed here. New RFID chips, nanoscale or sensor-enabled radio technologies and better sensor networks have been developed to take care of unexplored diseases, as well as for quality control of medicines, drugs, equipment and for monitoring of physiological parameters for better diagnosis and therapeutic treatment.

Development of the Sensor System

Development of some nano-sensors and systems[8-106] are described here :

HIFU System : HIFU (high intensity focused ultrasound is a good treatment technique of tissue problems[3-30]. The system gives off high frequency sound waves, to generate a strong beam to a specific part of a disease or cancerous region. The cells die with high intensity ultrasound beam kept focused directly onto them and cancer cells are killed with no side effects.

Mainly, the HIFU system can easily be used for the treatment of prostate cancer, kidney cancer, pancreatic cancer, liver cancer, bladder cancer and brain problems.

The HIFU has PZT-4 material for its transducer having frequency of 1 MHz [Figs. 1-2]. A new piezo-composite material developed locally has also been used to fabricate the high power therapeutic transducer. The specifications are as ultrasonic power upto 100 Watts and focal length as 12 cm. The schematic diagram of HIFU system is shown in in Fig. 1 and total system in Fig. 2 with excitation generator and output results from the cyst in the brain.

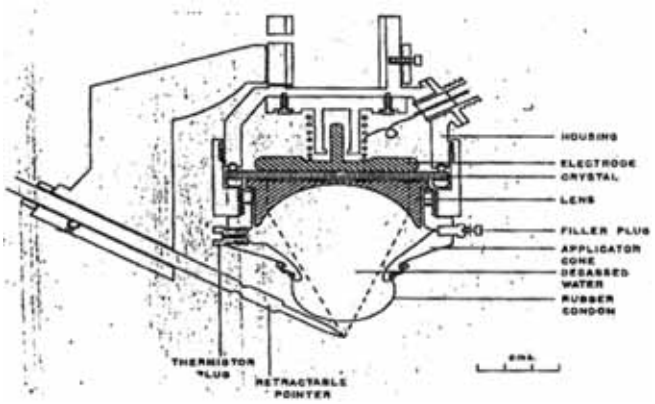

Fig. 1. Design details of HIFU system[7-9]

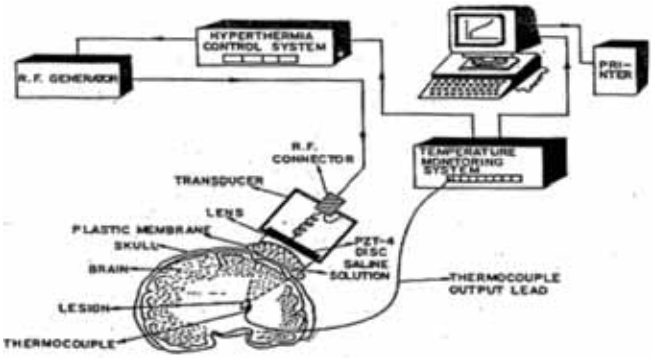

Fig. 2. High intensity focal ultrasound transducer with PZT disc, membrane and thermos-couple probe for temperature profile

Photograph shown in Fig. 3 describes the composite based ultrasonic transducer.

HIFU Working : With HIFU, an effect on the tumour in the tissue is produced to create heating, cavitation and mechanical forces, with the thermal and cavitation mechanisms[3-7]. The thermal heating is produced by absorption of ultrasonic energy by the tissue, to give a

Fig. 3. Photograph of Piezo-composite based high power ultrasonic transducer[7-9].

rise in temperature of the tissue, which is dependent on the intensity of the ultrasound energy and the acoustic (ultrasound) absorption coefficient of the tissue. The ultrasonic intensity at the beam focus is higher than that outside of the focus.This gives the generation of tissue temperature elevation, in the focal zone of the beam causing tissue coagulation and denaturing of the tissues well in time.

IOT-based Ultrasonic Systems for Health Care

Ultrasonic IOT in Health Care : The usage of the IOT technology in the healthcare applications[89-96] ensures the health care industries to enhance the quality of the care and minimize the expense with the automation and the resource optimization provided by it. The IOT in the medical imaging enables to have identification and the corrective measures to be taken in the real time with the auto analyzing of the imaging apparatus parameters at ease. Digitization reaching to many areas in the medical technology has also paved its way for the monitoring and the management of the medical equipment's, the internet of things in the medical imaging would reduce the waiting time and the vexation for the patients as well as the physicians. So the paper presents the review on the internet of things based medical imaging technology for the health care applications providing the significance of the internet of things in the medical imaging technology.

Internet of things (IOT) has manyhealth care applications[37] with minimum cost in health care industry, as Sapna *et al.*[38] reports IOT forrevolution in the healthcare avoiding the lack or the delay in the diagnosis, failures in the appropriate testing or the initiation in the follow up, the insufficiency to access the medical history of the patients, misconception and the wrong prescriptions, lack of knowledge about the person's previous medical records. The author S. Smys *et al.*[55,46] elaborates the topology of WSN in the IOT, and the applications and the protocols of the IOT. The latest development in the sensors also plays a significant role in IOT for the medical industry. IOT based sensing system is given in Fig. 4 and IOT based health monitoring plan is shown in Fig. 5.

Other IOT based sensor systems and applications: Smart health monitoring system using IOT based smart fitness mirror Moreover, an emotion-aware connected healthcare system[98-106] has used different IOT devices to measurement system that relies on an ultrasonic sensor.

- A layered IOT-based architecture for a distributed structural health monitoring system has been studied by F Lamonaca, C Scuro, and PF Sciammarella. IOT-based system, in[22] an ultrasonic inspection system for the SHM is proposed by[23], the Huang with Hilbert Transform which is used to analyse the sensor data to infer the health.
- An IOT-based waste management system and industrial waste materials monitored by cloud has

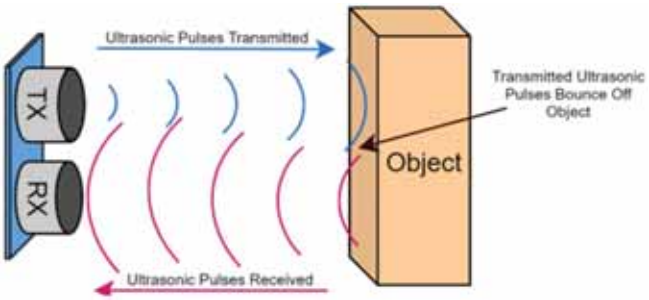

Fig. 4. (a) Ultrasonic sensing concept

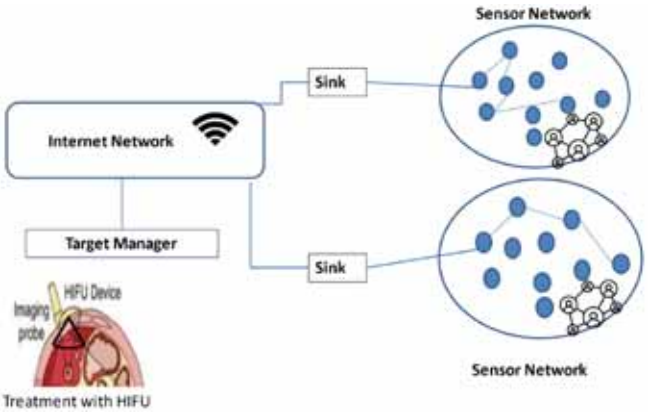

Fig. 4. (b) HIFU: Ultrasonic sensing concept

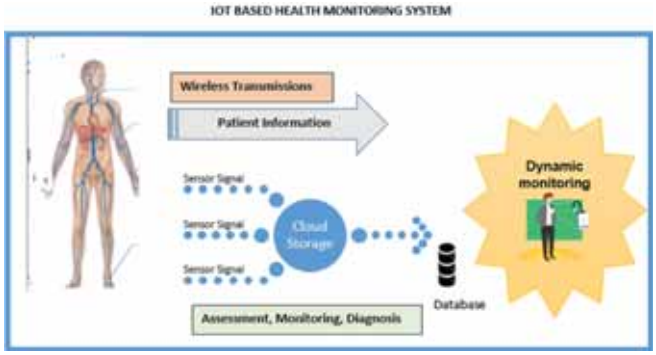

Fig. 5. (a) HIFU: Ultrasonic sensing concept

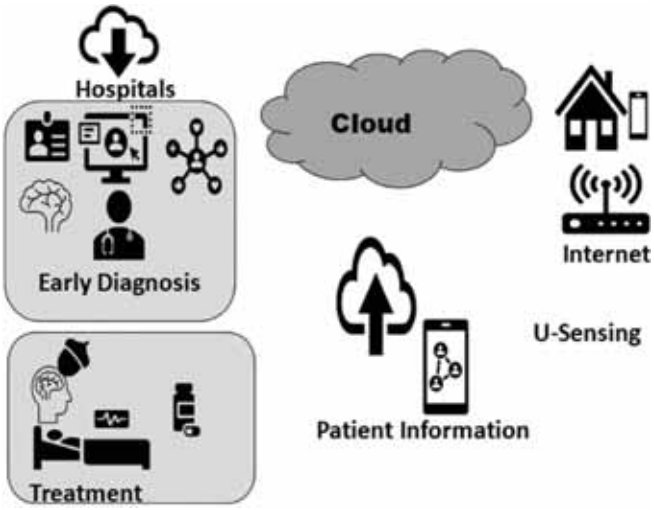

Fig. 5. (b) Layout of health monitoring system

been studied by D. Misra *et al.* Ultrasonic sensors are used for distance measurement with IOT approach to give IOT-based waste bins work effectively by using ultrasonic sensor systems into the IOT-based system.

- Novel implementation of IOT based non-invasive sensor system for real-time monitoring of intravenous fluid level for assistive e-healthcare has also been studied by PP Ray *et.al.*
- IOT based health care monitoring system for rural pregnant women has been developed by S.S. Amala *et al.*
- Awareness and access to a healthcare centre, equipped with modern maternity facilities. The side effects of long-term ultrasonic exposure on the fetal are, generally, not there,
- IOT based wearable healthcare system, for post COVID-19 use has been studied by C Chakraborty *et.al.* The important roles for IoT enabled healthcare systems are total communications for IOT based healthcare systems[56,59].

IOT based Medical Imaging : Medical imaging refers to the acquiring of the human body internal images for the diagnosis of the disease or treatment or research[90-98]. The medical imaging is one of the vital requirements in the hospital. The internet of things in the medical imaging enables the sharing, diagnosis and the retrieval of information in the real time and eludes the problem of repeated examinations, consultation difficulties and the misdiagnosing. Internet of Things with the medical imaging equipment's for the easy sharing of the images over the internet result in more accurate diagnosis and the treatment in real time.

The ultrasound scans are the medical imaging equipment utilized for the having a look on the inside of the body. They are the acoustic energy in the form of the waves with the frequency higher than the human hearing range and used in the analyzing the inside of the human body as proffered by the Nikolov, *et al.*[91] it finds its necessity in the medical imaging of the abdominal problems, uterus, the kidney problems and in the identifying the status of the baby in the fetus *etc*.

Medical imaging equipment are used for the diagnoses or in the detection of the disabilities, abnormalities, or disease in the human body. Due to increased number of the reports that lead to confusion, misplacing of the records and the wrong treatments, equipment can be embedded with the capability of the connecting to the internet to transfer the reports diagnosed, immediately to the concerned doctor and the patient over the internet, to reduce the patient waiting time, vexation as well as the misplacing of the records avoiding the wrong treatment. Such IOT enabled medical imaging equipment makes the monitoring of the patient, diagnosis of the disease and the management of the patients record easy.

Krishna, *et al.*[5], gives an "FPGA based computer aided system as a portable ultrasound imaging system for diagnosing the abnormalities in the kidney. The system includes a wireless unit in it to transfer the diagnosis over the internet to the cloud for the storage.

Chiuchisan *et al.*[6] the real time configurable medical imaging equipment based on the Verilog is utilized to have enhanced medical images Lu *et al.*[8] with the "technology of the IOT in the medical field, and in the management, monitoring and medical imaging.

The IOT in the health care industry provides a "visualization of the material management, digitization of the medical information and the digitization of the medical process. The internet of things (IOT) with the radio frequency identification ensures the eluding of the health care problems by supporting the production, distribution, and tracking of the medicines as well as the medical devices with the increase in the quality of the treatment and decrease in the cost of the management[74].

Cloud based Ultrasonic System

Recently, the cloud platforms are used in providing optimum performance, to be used as a solution to specific problemfaced by the client in daily life for the business or public life. Many cloud services are paid.Many transmission models such as Bluetooth, Zigbee, Wifi *etc*. are used for short-distance transmission while Sigfox, LTE *etc*. are used for long distance transmission to transmit the data to the cloud as a part of the internet of things (IOT).

IOT defines relationship between human and devices, anything that related to technology so that allowing entirely or some of the devices to connect between each other and perform the needed job without requiring in human to interact.

Cloud services are used as a monitoring platform to be used alongside with external hardware[90-106] like cloud computing with mobile devices[84-85]. Also, a protocol based on key agreement protocols is designed to help to secure data sharing and increase efficiency[86], or use of cloud computing with smartboard (Arduino) in IOT cloud[88]. An IoT cloud used to monitor healthcare using Arduino microcontroller[89-106] or to control smart garden watering system. The study of new pandemic coronavirus disease (Covid-19) fever detection method is according to World Human Organization (WHO) is human body temperature increase above the normal (37°C)[83-106]. Usually, a particular device used to measure the human temperature at airports, companies, hospitals, malls and many other locations.

Cloud-based U-sensing system with ultrasonic sensors is shown in Fig. 6. This very useful in the health care programs.

Blockchain Technology B in Healthcare

The growth in the use of blockchain technology in healthcare is progressing fast with significant impact on the healthcare industry[89-106]. In this work, the gap between the healthcare industry and blockchain technologies is required to be optimised. With the help of bibliometric analysis of dataset distribution, use of blockchain technology in healthcare becomes important. Case studies of telecare medicine information system and E-health are well accepted in terms of security and privacy to meet future challenges such as scalability and storage capacity, blockchain size, universal inter-operability and standardisation. Prospects in health data and sharing process, clinical trials, the pharmaceutical industry, big data, artificial intelligence, 5 G ultrasonic device, security and privacy are highlighted.

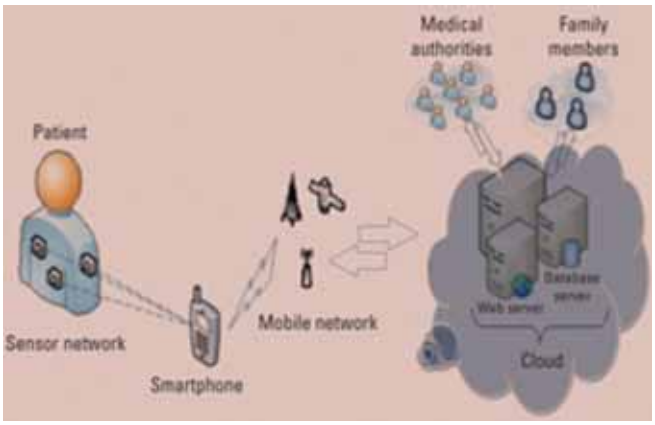

Fig. 6. Cloud-based U-sensing with ultrasonic sensors

IOT phenomenon has provided an incredible service to a wide range of healthcare systems and an AI-enabled and 5 G ultrasonic system for emergency patients who require ultrasound. Blockchain is generally used for Indian supply chain ecosystem.

AI (Artificial Intelligence) in Ultrasonic Systems

In AI (Artificial Intelligence), Artificial neural networks (ANNs) are biologically inspired computational models that are developed based on the networks of neurons in the human brain. Different types of neural networks have been developed for various applications of ANN in Science, Engineering, Medicine and Business. A neural network with some level of complexity, usually at least two layers, is called as a deep learning network, which can be used for imaging applications, say by using MATLAB programming[88-100].

AI based ultrasound system on a chip is shown in Fig. 7. This is called Butterfly iQ, (107) and is a cheap

Fig. 7. AI based ultrasound system on a chip (by Johnson, IEEE Spectrum news, 2021)

hand-held ultrasound tool with AI smarts tucked inside. This gadget will revolutionise medical imaging in hospitals and clinics, change the game in global health to become a consumer product of ubiquitous.

Results : Case Studies / Applications

Nano-Ultrasonic Sensors and IOT systems for Biomedical Applications : Recent nano-ultrasonic sensors and IOT systems have been discussed[91-106] for healthcare applications by V.R. Singh, Life Fellow-IEEE, National Physical Laboratory, New Delhi, India, in his IEEE DL- Talk on 17 September 2021 03:30 PM to 04:30 PM (Australia/Sydney), https://events.vtools.ieee.org

Development of new nano-ultrasonic and nano-acoustic sensor systems is important for the measurements in a reliable manner for remote monitoring as well as for controlling of the health, in particular, in old age patients living in remote and hilly areas. Advanced acoustic/ultrasonic biomedical sensors and IOT based systems are discussed for healthcare applications, with the main emphasis on tele-health program. The newly developed diagnostic and therapeutic devices use RFID chips, nano-scale or sensor-enabled radio technologies and/or sensor networks. These are useful for solving the problem of unexplored diseases, as well as for controlling of the quality of medicines, drugs, equipment and physiological event monitoring systems. WSN (Wireless Sensor Networking) is preferred to be used with the sensing devices for remote applications. Cancer hyperthermia and focal ultrasound therapy for the treatment of deep-seated brain tumours are case studies.

Nano-Ultrasonic Sensors in IOT -based Systems for Healthcare Applications : Importance of nano ultrasonic sensors in IOT systems for Healthcare Applications[96-109] has been discussed by V.R. Singh during the IEEE Systems/NTC DL-Talk, at Houston-USA, Galveston Bay Section of IEEE, Joint Societies Chapters, 2020 IEEE Inc. Galveston Bay Section, on Friday, March 26th, 2021 10:00 AM- 11:00 PM US-CDT (Houston), https://site.ieee.org/gb/ ONLINE Virtual Meeting, IEEE_GBS_03262021in by VR Singh

Biomedical acoustic imaging sensors for U-health are described in ICA-2016 by V.R. Singh, http://www.ica2016.org.ar › ICA2016-1135

Nano-PZT. (Lead Zirconium Titanate), quartz and other such piezoelectric materials are cited for the development of nano-ultrasonic sensors.

Advanced acoustic/ultrasonic biomedical sensors and IoT-based systems are presented for healthcare applications, with the main emphasis on telehealth, with newly developed systems. https://meetings.vtools.ieee.org ›

Paul C. Lauterbur has described ultrasonic sensors; acoustic sensors; ultrasound transducers and micro/nanosystems, while K Lee has discussed Ultrasound imaging; Wearable and mobile ultrasonic sensors; Ultrasonic biosensors; Ultrasounds in cell sensing; Multimodal sensing and imaging systems. Novel Nanoporous Materials for Efficient Ultrasonic Biomedical Sensors "Nano-piezoelectrics" for sensor applications in 2016. https://www.mdpi.com › journal › ultrasonic-sensors-tra.

Biomedical acoustic imaging sensors for U-health, ICA 2016, http://www.ica2016.org.ar › ICA2016-1135, have been discussed by VR Singh where Nano- PZT. (Lead Zirconium Titanate), quartz and other such piezoelectric materials are used for the development of nano-ultrasonic sensors.

Nano-UltrasonicTele-systems : New nano-ultrasonic and nano-acoustic sensor systems are developed for measurements in a reliable manner for remote monitoring and control of the health of say, old age patients living in remote or hilly areas. Advanced acoustic/ultrasonic biomedical sensors and IOT based

systems are presented for healthcare applications, with main emphasis on tele-health. The newly developed diagnostic and therapeutic devices, generally, by using RFID chips, nano-scale or sensor-enabled radio technologies and appropriate sensor networks would be easily used in solving the problems of mainly unexplored diseases, as well as for controlling of the quality of medicines, drugs, equipment and physiological event monitoring systems. WSN (Wireless Sensor Networking) is used here with the sensing devices for remote application, described by Smith *et al.* while 1,3 Design and fabrication of nanoscale ultrasonic transducers: have been discussed by Richard Smith *et al.* in detail and recent developments in biomedical sensors are given by A. Mehmet Engine *et al*.

Piezoelectric Micro-machined Ultrasound Transducer (PMUT) Arrays for Integrated Sensing, Actuation and Imaging has been described by Y. Oiu *et el*. have given low power transducers and transducer arrays integrated with electronic systems. Generally, piezoelectric micromachined ultrasound transducers which are diaphragm-like thin film flexural transducers are formed on silicon substrates as integrated transducer arrays. Microfabrication technique is used to develop such devices with electrical interconnection and integration on-chip electronics, with tunable frequency.

Tissue Phantom for Calibration of Ulttrasonc Sensors has been discussed by S. Yadav *et al*. Tissue phantoms are, generally, used in the calibration of therapeutic and diagnostic systems. Thus, Tissue-Mimicking (TM) phantoms are developed and studied here for various ultrasonic output parameters. These phantoms have been developed by using agar-based Tissue-Mimicking Materials (TMM) with alumina as an absorption material. A pulser-receiver (make Panametrics, Model-5800, Waltham, MA 02154, USA) has been used to measure ultrasonic velocity and attenuation coefficient, which were found to be 1540-1550 m/s and attenuation 10.0-35.0 dB/m-MHz at frequencies from 2.5 MHz to 5.0 MHz. These ultrasound test phantoms incorporating TM material are useful in the performance evaluation of medical ultrasound systems.

An overview of biomedical sensors is given as the key component in various medical diagnostic instruments, detection sensors, drug analysis and screening sensors, and micro-nano-systems, in. Nano Magazine, https://nano-magazine.com › news.

Future Ultrasound Nano Technologies

Nano- biosensing systems for intelligent healthcare and COVID-19 management : Generally, biosensors are used as diagnostic tools for disease at early stage for health care, to correlate biomarker with disease pathogenesis. Nanotechnology is used for sensing unit fabrication, device integration, interfacing, packaging, and sensing performance at point-of-care (POC) as diagnostics for disease analysis and patient disease profile study, with bio-sensing as a non-invasive disease diagnosis[98-107].

Thus, such intelligent diagnostic tools are used to control COVID-19 pandemic disease which is a life-threatening respiratory infectious disease, where a rapid, selective and sensitive detection of human beta severe acute respiratory system coronavirus (SARS-COoV-2) protein is the key factor.

Covid-19 fever symptom detection based on IoT cloud : A new method of detection Covid-19 fever symptoms depending on IoT cloud services to solve the higher time delay of checking the crowded clients that enter public or private agencies which can lead to a dangerous field to spread the disease. using a practical experiment is developed using ultrasonic (SR-04), RFID (RC522), human body temperature (MAX30205) sensors, hardware used to transmit the received data (human temperature sensor) from the (MAX30205) to the cloud platform and collected data reached a critical value that specified previously and automatically take action to solve this situation.

Cerebras' New Monster AI Chip Adds 1.4 Trillion Transistorsextends to 7-nanometer process boosts the second-generation chip's transistor count to 2.6-trillion. IEEE Spectrum, Tech Alert, December 23, 2021, pp 1-2.

Artificial intelligence (AI) algorithms require powerful and efficient computer architectures for two distinct tasks: training and inference. The first is extremely compute- and memory-intensive, and in some cases can take days or weeks to complete. The latter usually implies real-time performance. As an increasing number of smart devices come online, performing more AI inference at the edge (far away from the cloud), they have the power to enable lower latency, greater privacy, better data governance, and higher availability when compared to cloud/data center-based inference. Training is a new federated learning computational models that perform

part of the training concurrently on each edge node and merge parameters on the cloud/server later. These findings interaction of hardware and software in edge architectures create innovate the ever-increasing energy efficiency, performance, and usability of AI systems at the edge.

This special issue of IEEE Micro will explore academic and industrial research combining AI and edge computing. These findings relate to the design, performance, or application of microprocessors and microcomputers.

IOT based Wearable Healthcare Systems and Study of Post COVID-19 : Flexible wearable sensors are used for IOTbased continuous health monitoring systems, in flexible mode (94-107).

Conclusion and Significance

Nano-ultrasonic sensors and IOT based systems have been described with their working principles, design aspects and possible healthcare applications. Development of different types of sensors and instrumentation systems has been given, by covering mainly. piezo-electric/ultrasonic sensors, bio-chip-based, biologically inspired sensors, bone devices, and *etc*. IOT- based and AI based sensing systems have also been discussed for mainly for health care applications. Future of nano-sensors and IOT systems with cloud technology, artificial intelligence and block-chain technology is discussed, for novel investigations like detection and treatment of alarming problems and diseases Corona-virus, *etc*.

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An ultrasonic exploration of physico-chemical properties for mixtures of dichloroacetyl chloride with polar, non-polar and polymers at 300 K

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The present study is oriented towards the demonstration of physico-chemical properties and molecular interactions of the prepared binary mixture of Dichloroacetyl chloride (DCAC) with methanol/ethanol/CCl_4/ PEGs through ultrasonic non-destructive characterization. The intermolecular interaction, structural ordering, and corrosiveness aspects of prepared binary mixtures have been interpreted on the basis of measured (density, viscosity, ultrasonic velocity) and estimated thermo-physical quantities (compressibility, free length, free volume, Gibb's free energy, thermal relaxation time, and ultrasonic absorption) at 300K. All binary mixtures have been received to undergo exothermic reaction during preparation while mixture DCAC + methanol has been found to produce excessive heat and harmful odour vapour. The study confirms that DCAC+CCl_4 consist of least intermolecular interaction while mixture DCAC with PEG600 possesses strong molecular interaction among constituents accomplished by intense hydrogen bonding and physical forces. It also concludes that DCAC + PEG600 shall be highly viscous and least corrosive in comparison to other prepared mixtures. The present study provides new dimension for applicability of hazardous chemical DCAC in mixture form toward herbicides, pesticides, and fertilizers industries.

Keywords: Binary liquid mixture, intermolecular interaction, physico-chemical properties, ultrasonic parameters.

Introduction

To understand the nature and strength of molecular interactions among the molecules of liquid mixtures, physico-chemical properties of liquid are very advantageous. These properties of mixtures are very helpful to design environmental friendly chemical products and minimizing the hazardousness of materials in the chemical and pharmaceutical industries[1-3]. Study of volumetric, thermodynamic and viscometric properties of multi-component liquid mixtures provides foundation for chemical synthesis for industrial applications. In the field of chemicals and pharmaceuticals binary liquid mixtures have been found enormous applications. Ultrasonic characterization provides underlying information about the molecular interaction of liquids and solids, due to its ability to characterize the physico-chemical behaviour of the medium[4,5]. Thermo-physical properties of mixtures also provide valuable information about solute-solute and solute-solvent interactions[6-8]. Differences in molecular size, molar mass, temperature, pressure and mole fraction of constituent liquids in binary mixtures is the cause of non-linear deviations in density, viscosity and velocity, with ideal values for them. The variation in thermo-physical parameters and their additional values with structure provides an insight into the molecular process by investigating molecular interactions[9-12].

Dichloroacetyl chloride (DCAC) is an acyl chloride that is obtained through the displacement of the hydroxyl group of dichloroacetic acid by chloride. It is a polar and colorless liquid having pungent odor vapors that are irritating to eyes with mucous membranes and

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belongs to the corrosive, flammable, and reactive hazard class. It has a role as a hapten (a compound which, when coupled with a protein or other molecules, can cause the formation of antibodies) and it is also the precursor to antibiotics, including chloramphenicol[13,14]. It is used not only in the manufacturing of fertilizers, pesticides, agrochemicals but also in preventing, destroying, and instigating pests.

Alcohols ($C_nH_{2n+1}OH$) are the organic polar compound that carries at least one (?OH) bound to saturated carbon atoms which are used as drugs. Methanol and ethanol are the simplest members of the alcohol family. The chemical and thermo-physical properties of Methanol/ethanol with nitriles, pyridine, dodecane, dimethylformamide, tetrahydrofuran, trichloromethane, ethyl acetate, methyl acetate, N, N-dimethylformamide, nitrobenzene, triethylamine has been reported in the literature[15-25].

Carbon tetrachloride (CCl_4) posesses non-polar, colorless, highly toxic, and non-flammable nature with intense odor characteristics. It belongs to the group of organic halogen compounds which is useful as fire sedative, refrigeration fluid, propellant etc. It is water-insoluble whereas compoundable with ethyl alcohol, ether, benzene, chloroform, and most other organic solvents. Intermolecular interaction studies on the basis of density, viscosity and ultrasonic velocity for liquid mixtures of CCl_4 with various chemicals have been reported elsewhere[26-32].

PEG have wide application in the field of food, pharmaceutical, cosmetic (skin cream), chemical industries, etc. due to environmental friendly nature with low toxicity, water solubility and excellent bio-compatibility[33,34]. Polyethylene glycols of different molecular weight as 200,400 and 600 are also known as PEG200, PEG400, and PEG600, respectively. Due to having –O– and -OH groups in the identical molecule, PEG consists of good proton donor and acceptor ability. This feature makes it compatible to form inter- and intra-molecular hydrogen bonding with other molecules[2]. Due to excellent properties, PEG can also be used in the fuel gas desulfurization. The thermo-physical study of PEG200/400/600 with dimethyl sulfoxide, tetrabutylammonium bromide, o-cresol, benzene and toluene, 2 butanol, cyclic ether, water and ethanol, ionic liquid, ionic liquid BMIBF4, water, ethanolamine, m-Cresol and aniline have been narrated in the literature using ultrasonic technique[33-46].

No work has been done for binary mixture of Dichloroacetyl chloride with methanol/ethanol/CCl_4/PEGs in the literature using ultrasonic non-destructive testing whereas they have a significant role in the field of chemical industries. Hence, the present study is concentrated on ultrasonic characterization of binary mixtures containing DCAC and methanol/ethanol/CCl_4/PEGs at 300K and 100.5 kPa to find out physico-chemical characteristic related to molecular interaction. On the basis of ultrasonic and related thermo-physical parameters, molecular interaction and characteristic features of prepared binary mixtures have been explored at 300K.

Synthesis

The chemical Dichloroacetyl chloride has been considered as solute to make the binary mixture. The DCAC and Polymer (PEGs) has 98% purity and has been manufactured by Sigma Aldrich Chemical Pvt. Ltd. Bangalore India and Thomas Baker Pvt. Ltd., Mumbai, India respectively whereas the chemicals methanol/ethanol, carbon tetrachloride (CCl_4), and PEG200/400/600 have been taken as polar, non-polar and polymer solvents, respectively for the preparation of the binary mixture. The methanol and ethanol contain 99.5% and 99.9% purity, respectively and have been manufactured by Sigma Aldrich Chemical Pvt. Ltd. Bangalore India while CCl_4 have 99% purity and have been manufactured by Molychem Chemicals Pvt. Ltd. Mumbai, India. The basic specifications of the chemicals used in the study are listed in Table 1, while their chemical structures are depicted in Fig. 1.

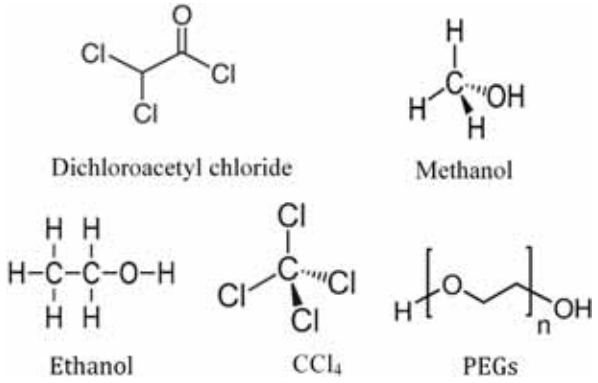

Fig. 1. Chemical structure of the studied Compound

The binary mixtures have been prepared by taking the solute and solvents in volume by volume ratio 47. The Dichloroacetyl chloride (20%, 6 mL) and methanol/ethanol/CCl_4/PEGs (80%, 24 mL) have been taken as

Table 1 – Details of Used Chemicals (Chemicals/formula, CAS number, Molar mass, Source, Mass fraction purity, Water content and Analysis method).

Chemicals/formula	CAS Number	Molar mass ($g.mol^{-1}$)	Source	Mass fraction purity (%)	Water content (Mass %)	Analysis method
Dichloroacetyl chloride ($CHCl_2COCl$)	79-36-7	147.38	Sigma Aldrich Chem. Pvt.Ltd. Bangalore, India	98	Not detected	KF#
Methanol (CH_3OH)	67-56-1	32.04	Sigma Aldrich Chem. Pvt.Ltd. Bangalore, India	99.5	0.02	GC*
Ethanol (C_2H_5OH)	64-17-5	46.07	Sigma Aldrich Chem. Pvt.Ltd. Bangalore,India	99.9	0.02	GC*
Carbon tetrachloride (CCl_4)	56-23-5	153.82	Molychem Chem. Pvt. Ltd Mumbai, India	99	0.02	GC*
PEG200 ($H(OCH_2CH_2)_nOH$)	25322-68-3	200	Thomas Baker (Chem.) Pvt. Ltd. Mumbai, India	98	0.30 ± 0.02	KF#
PEG400 ($H(OCH_2CH_2)_nOH$)	25322-68-3	400	Thomas Baker (Chem.) Pvt. Ltd. Mumbai, India	98	0.36 ± 0.02	KF#
PEG600 ($H(OCH_2CH_2)_nOH$)	25322-68-3	600	Thomas Baker (Chem.) Pvt. Ltd. Mumbai, India	98	0.46 ± 0.02	KF#

* Professed by supplier, #Karl Fischer titration method.

constituents to form six samples from 30 mL of binary mixture. All the binary mixtures, during preparation, have been found to be highly exothermic. The highest exothermic nature is observed for the mixture of DCAC with polar solvent methanol. Since chemical DCAC evaporates noxious odour vapours which are harmful and hazardous to the eyes with mucous membranes and also it's very low amount produces a high exothermic reaction, therefore the low percentage of it has been taken to make the binary mixture.

The water content in Dichloroacetyl chloride and PEGs was determined by Karl Fischer titration method (Model no. KAFI-KF12240121, LABINDIA). In the process of titration, mixture of SO_2, I_2 and pyridine have been used as KF reagent while dry methanol as solvent. The water content in constituent liquids is presented in Table 1. Purchased chemicals have not undergone any purification prior to preparation of binary mixtures. All the samples have been prepared at 300K and 1atm. The measurement of pressure has been done

Table 2 – Mole fraction of constituents in binary samples of Dichloroacetyl chloride with methanol/ethanol/CCl4/PEGs at 300K and atmospheric pressure (100.5kPa).

Samples	Abbreviation ↓	Components ↓	Mole Fraction
Dichloroacetyl chloride + Methanol	S_1	DCAC	0.0961
		Methanol	0.9039
Dichloroacetyl chloride + Ethanol	S_2	DCAC	0.1337
		Ethanol	0.8663
Dichloroacetyl chloride + CCl_4	S_3	DCAC	0.2038
		CCl_4	0.7962
Dichloroacetyl chloride + PEG200	S_4	DCAC	0.3269
		PEG 200	0.6731
Dichloroacetyl chloride + PEG400	S_5	DCAC	0.4907
		PEG 400	0.5093
Dichloroacetyl chloride + PEG600	S_6	DCAC	0.5890
		PEG 600	0.4110

by digital Barometer and found to be 100.5 kPa. The uncertainty was found in pressure measurement in present study is ± 0.15 kPa. The mole fraction of constituents in prepared mixtures is listed in Table 2.

Experimental

Density Measurement

The densities of binary liquid mixtures were determined using the density bottle method at 300K and atmospheric pressure 100.5 kPa. For this, density bottle (25 mL) with tolerance capacity ±0.8/mL and digital electronic balance having accuracy ±1 10^{-3}g have been used. The density bottle is calibrated by distilled water (0.9965 g.cm^{-3})[2,5]. The uncertainty in density *(ρ)* and temperature measurements are ±1 10^{-3} g.cm^{-3} and ±0.1°C respectively.

Viscosity Measurements

The determination of viscosity *(η)* of prepared mixtures has been performed by Poiseuille method[2,49,50]. The measurement was completed by observing the outflow time of fixed volume of samples with capillary thin tube using digital stopwatch (accuracy-0.01s). Distill water (viscosity-0.8502 mPa.s) was used as reference fluid in estimation of mixture viscosity[2,5]. The sample temperature was maintained by water bath thermostat (accuracy- ±0.1°C). The uncertainty in measured viscosity is ±2.1%.

Ultrasonic velocity Measurements

The ultrasonic interferometer has been use to measure the ultrasonic velocity *(U)* of the liquid mixtures. The credibility of measurements have been checked by receiving sound velocity data for distill water at 300K[4,5]. The present sound velocity in distill water at 300K has been observed 1502.5 ± 0.6 m.s^{-1} while the reported values of it at 298K and 301K are 1496.65 ± 0.1 m.s^{-1} and 1504.29 ± 0.1 m.s^{-1}, respectively[2,51]. The uncertainty in present velocity measurements is ±0.6 m.s^{-1}.

Theoretical Aspects

Thermo-physical Parameters

Isentropic/adiabatic Compressibility

Intermolecular association and orientation of the solvent molecules around the solute molecules can be described on the basis of isentropic compressibility. The compressibility of the binary mixtures can be determined using the following expression[1-3,5].

$$\beta = \frac{1}{U^2 \rho} \tag{1}$$

Intermolecular Free Length

Determination of free length in liquids and liquid mixtures has been subject to a semi-empirical relation to obtaining the intermolecular free length. The free length is the separation between the surfaces of adjacent molecules of the binary mixture. The free length can be determined by following Jacobson relation[1-2].

$$L_f = K_T \beta^{1/2} \tag{2}$$

where, K_T is the constant and its values is 198 × 10^8.

Free volume

Free volume *(V_f)* is defined as the average volume in which the center of the molecules can move inside the hypothetical cell due to the repulsion of the surrounding molecules. The determination of the free volume of a binary mixture can be determined using viscosity *(η)*, ultrasonic velocity *(U)* and effective molar mass *(M_{eff})* of that mixture[2,4].

$$V_f = \left(\frac{M_{eff} U}{\eta K} \right)^{3/2} \tag{3}$$

where, constant K has value is 4.28 × 10^9.

Thermal Relaxation Time

The relaxation time *(τ)* is the time in which the structural deformation by propagation of ultrasonic wave is restored in the medium through translational motion. It depends on the temperature and impurities and can be evaluated using the following relation[1-5].

$$\tau = \frac{4}{3} \beta \eta \tag{4}$$

Gibb's Free Energy

The energy involved in the formation of binary mixture with constituents through structural relaxation process is measured by Gibb's free energy. The Eyring-salt process theory provides following expression for the Gibb's free energy and thermal relaxation time[1-2].

$$\Delta G = -KT \log \left(\frac{h}{KT\tau} \right) \tag{5}$$

Ultrasonic Absorption

The loss of energy of ultrasonic waves by the concerned medium is called ultrasonic attenuation. The ultrasonic absorption/attenuation over frequency square

(α/f^2) in a binary mixture can be calculated theoretically using the following expression[1-5].

$$\left(\frac{\alpha}{f^2}\right) = \frac{8\pi^2\eta}{3\rho U^3} \quad (6)$$

Results and Discussion

The measured density, viscosity and ultrasonic velocity for pure liquids (Dichloroacetyl chloride, methanol/ethanol/CCl4/PEGs) are shown in Table 3 and are found very close to reported values given in the literature[20,21,29,30,32,41,43,44]. Therefore, our measured quantities are justified. The same measured quantities for binary mixtures of DCAC with methanol/ethanol/CCl_4/PEGs are given in Table 4 and presented in Figs. 2-3. The acoustical and thermo-physical parameters of the prepared binary samples are estimated through measured quantities and Eqs.1-6 which are presented in Table 5 and depicted in Figs. 3-6.

The measured density has been observed to decay slowly for polar-polar mixtures (S_1 to S_2) with an increase in molar mass while it increases very rapidly for polar + non-polar mixture (S_3), and finally, it decreases and saturates with molar mass for polar + polymer mixtures (S_4 to S_6) [Fig. 2]. The decrease in density from mixture S_1 to S_2 indicates that accommodation of solute molecules between the intermolecular spacing of solvent decays with enhancement in the molar mass of polar solvent. An intense increase in density for the polar + non-polar mixture (S_3) confirms that accommodation of DCAC within non-polar solvent shall be high. The density for polar + polymer mixtures (S_4 to S_6) is found to be in between the densities of polar + polar and polar + non-polar binary liquid mixtures under study. This reveals that the compactness of molecules for polar + polymer mixtures shall lie in between both other types of mixtures formed with DCAC. The density of polar + polymer mixture (DCAC+PEG200/400/600) is observed to enhance slowly with molar mass, which indicates that the bonding between constituent liquids enhances with molar mass of polymer solvent. The variation of density with a molar mass of all three types of mixtures has been found to follow a non-linear curve.

Table 3 – Density, viscosity and ultrasonic velocity for constituents of prepared binary mixtures at fixed mole fraction of each solute/solvent.

Components ↓	T (K)	Density (10^3 kg m^{-3})		Viscosity (mPa.s)		Velocity (m s^{-1})	
		Present	Lit.	Present	Lit.	Present	Lit.
Dichloroacetyl chloride	300	1.532	1.532 (at 298K)	1.266	-	934	-
Methanol	298	-	0.7863[20]	-	0.551[20]	-	1108[20]
	300	0.783	-	0.531	-	1086	-
	303	-	0.7824[21]	-	0.508[21]	-	1088[21]
Ethanol	298	-	0.7843[20]	-	1.084[20]	-	1144[20]
	300	0.776	-	1.054	-	1132	-
	303	-	0.7812[21]	-	0.987[21]	-	1128[21]
CCl_4	298	-	1.584[29]	-	0.821[29]	-	0.918[29]
	300	1.562	-	0.879	-	916	-
	303	-	1.559[32]	-	0.768[30]	-	0.906[32]
PEG200	298	-	1.0086[43]	-	-	-	1535.5[43]
	300	1.070	-	40.249	-	1540.0	-
	303	-	1.116[44]	-	38.72[41]	-	1567.7[44]
PEG400	298	-	1.0191[43]	-	-	-	1572.5[43]
	300	1.079	-	71.224	-	1576.3	-
	303	-	-	-	69.62[41]	-	-
PEG600	298	-	1.0289[43]	-	-	-	1605.7[43]
	300	1.088	-	96.344	-	1607.0	-
	303	-	-	-	101.7[41]	-	-

Viscosity is received to resemble the opposite nature of the molar mass-dependent density of three types of samples. It is clear from Table 4 and Fig. 2, that the viscous/internal frictional force will be large for the binary mixtures DCAC with PEGs while it will be least for mixture of DCAC with methanol. The viscosity characteristic also informs that the shear stress and lateral forces among molecules will be high for mixture of polar DCAC and polymer PEGs. The enhancement in viscosity with molar mass for polar + polymer mixture (Fig. 2) is caused by strengthening of lateral bonding between constituents. The low viscosity for polar + non-polar mixture (DCAC + CCl_4) in comparison to the polar-polymer mixture confirms the presence of weak shear forces. The viscosity of the polar + polar mixture is found very close to the viscosity of the polar + non-polar mixture.

The velocity of ultrasonic wave has been found lowest for mixture S_3 (DCAC + CCl_4) while a continuous enhancement in it for the polar-polar and polar-polymer mixtures (S_1 to S_2 and S_4 to S_6) has been obtained (Table 4 and Fig. 3). The ultrasonic velocity is directly proportional to the square root of the bulk modulus. The quantity bulk modulus measures the amount of internal stress/force per unit strain. Therefore, ultrasonic velocity provides a direct consequence of the strength of bonding among the molecules. The lowest velocity for the mixture of DCAC + CCl_4 confirms the existence of the weak intermolecular interaction. Hence, the strength of physical forces acting among molecules of DCAC + CCl_4 mixture shall be feeble. The comparatively high ultrasonic velocity for polar-polar mixture explores the existence of relatively strong bonding among the constituents. An increase in the ultrasonic velocity of polar + polymer mixtures (S_4 to S_6) confirms the presence of strong bonding network between DCAC and PEG. The bonding network shall be more strengthen and directional for the mixture of DCAC with PEG600 as velocity for it is observed high.

The compressibility is found to decrease continuously in polar + polar, polar + non-polar, and polar + polymers with the molar mass of mixture (Table 5). This indicates that the mixture of DCAC with PEG600 shall be least compressible. The free length defines the average space

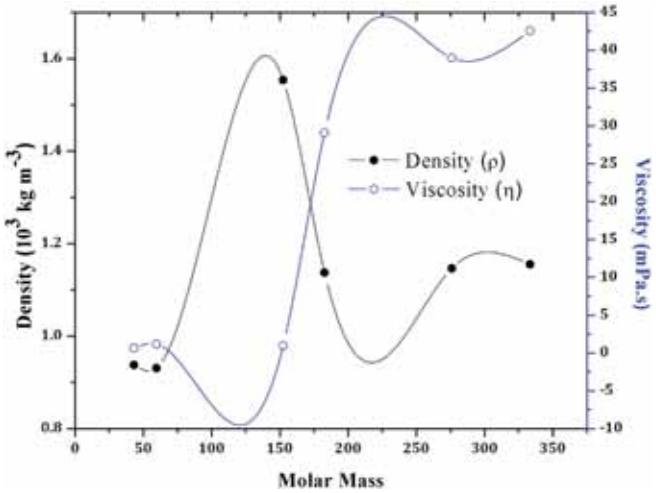

Fig. 2. Density and Viscosity vs. Molar mass of binary mixtures at 300K

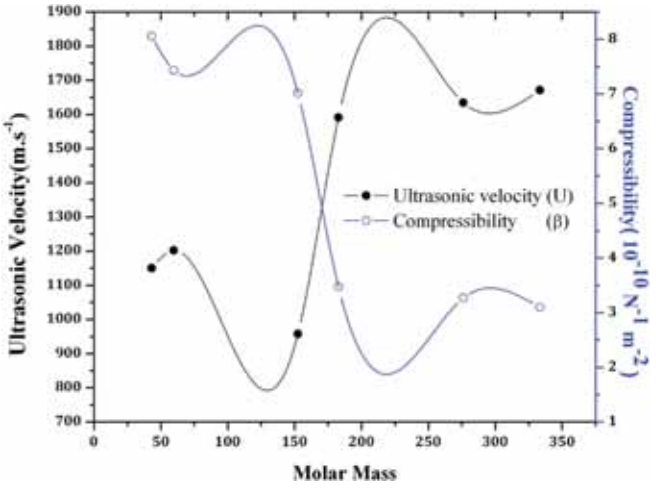

Fig. 3. Ultrasonic Velocity and Compressibility vs. Molar mass of binary mixtures at 300K.

Table 4 – Measured quantities of binary mixture of DCAC with methanol/ethanol/CCl_4/PEGs at 300K.

Binary Samples → Properties ↓	S_1	S_2	S_3	S_4	S_5	S_5
Molar Mass (g.mol^{-1})	43.126	59.611	152.508	182.797	276.046	333.405
Density (10^3 kg m^{-3})	0.938	0.931	1.554	1.137	1.146	1.156
Viscosity (mPa.s)	0.634	1.160	0.958	29.100	39.007	42.408
Ultrasonic velocity (m s^{-1})	1150.4	1202.2	957.6	1591.5	1634.8	1671.2

Table 5 – Calculated value of compressibility *(β)*, free length *(L_f)*, free volume *(V_f)*, thermal relaxation time *(τ)*, Gibb's free energy *(ΔG)*, and ultrasonic absorption *(α/f^2)* of DCAC and methanol/ethanol/CCl_4/PEGs at 300K and atmospheric pressure (100.5 kPa).

Samples ↓	Molar Mass	β	L_f	V_f	τ	ΔG	α/f^2
		$10^{-10}N^{-1}m^2$	$10^{-10}m$	$10^{-10}m^3mol^{-1}$	$10^{-12}s$	10^{-21} J. mol^{-1}	10^{-17} Np $s^{-2}cm^{-1}$
S_1	43.126	8.057	5.620	781.780	0.681	2.606	11.675
S_2	59.611	7.435	5.398	548.410	1.149	3.548	18.862
S_3	152.508	7.017	5.245	2125.700	0.896	3.100	18.458
S_4	182.797	3.472	3.689	35.700	13.470	7.975	166.900
S_5	276.046	3.263	3.577	44.442	16.975	8.391	204.760
S_6	333.405	3.098	3.485	53.407	17.602	8.456	207.700

Standard uncertainties $u(M_w)$ = ±5.1%, $u(\beta)$ = $\pm0.001\times10^{-10}N^{-1}m^2$, $u(L_f)$ = $\pm0.001\times10^{-10}$ m,
$u(V_f)$ = $\pm0.001\times10^{-10}m^3mol^{-1}$, $u(\tau)$ = $\pm0.001\times10^{-12}$ s, $u(\Delta G)$ = $\pm0.001\times10^{-21}$ joule mol^{-1} and $u(\alpha/f^2)$ = $\pm0.001\times10^{-17}$ Np.$s^{-2}cm^{-1}$

among atoms (atomic separation) and is well correlated with compressibility. The significant interaction among constituent molecules of binary mixture enhances the compactness between solute and solvent and settles low atomic separation and compressibility. Therefore, the trends of molar mass dependent free length and compressibility have been found same for present mixtures (Figs. 3-4).

The free volume of polar + polar mixture (S_1 to S_2) is found to decrease with an increase in the molar mass of solvent (Fig. 4) while for polar + non-polar mixture (S_3) it rapidly increases in comparison to polar + polar mixture and hereinafter it is observe to decrease for polymers and tends to saturate with enhancement in molar mass. Decay in free volume for S_1 to S_2 indicates, the accommodation of solute molecules between the intermolecular free space of solvent has been decaying. For polar + non-polar mixture (S_3), an acute enhancement in free volume is seen which confirms that accommodation of solute within non-polar solvent shall be high. Similar result has been reported in the literature for mixture of toluene + CCl_4[17]. Comparatively, the low free volume has been obtained for the present polar-polymer mixture (S_4 to S_6) that increases slightly with molar mass. The overall variation of free volume with molar mass of mixtures is found to follow the characteristic of density.

The thermal relaxation time and Gibb's free energy are observed to increase with solvent molar mass in polar + polar mixture (S_1 to S_2) and polar + polymers (S_4, S_5 and S_6) which is shown in Fig. 5. But for polar + non-polar mixture (S_3), both the parameters received to

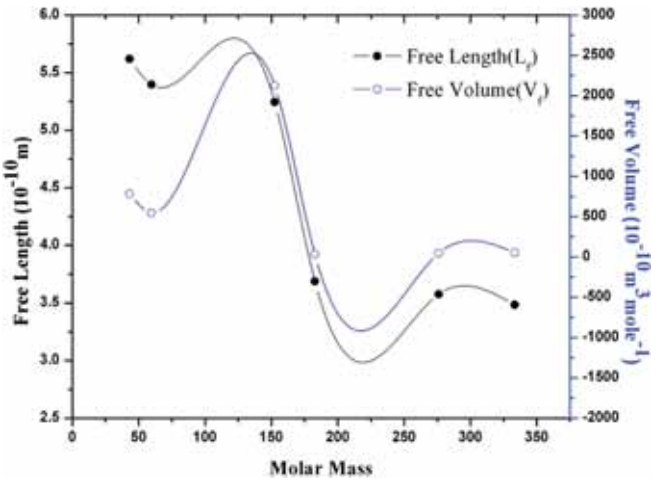

Fig. 4. Free Length and Free volume vs. Molar mass of binary mixtures at 300K.

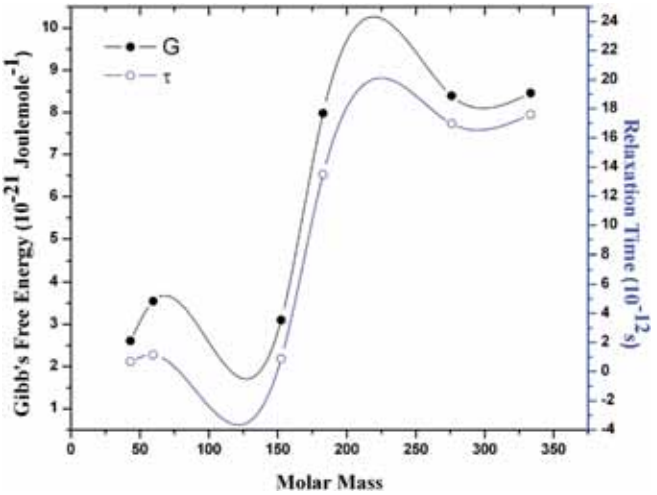

Fig. 5. Gibb's free energy and Th. Relaxation time vs. Molar mass of binary mixtures at 300K.

decrease slowly with increase in molar mass of mixture. The thermal relaxation time is well correlated with viscosity and compressibility of liquid. The compressibility is receive to decay with the molar mass while viscosity is received to enhance in the polar + polar mixture and polar + polymer mixture. But for polar + non-polar mixture, the viscosity is somewhat low. Therefore, both of these parameters together affect molar mass dependent thermal relaxation time in polar + polar, polar + non-polar and polar + polymer mixtures. The structural relaxation process for rearrangement of molecules in present mixture with hydrogen bonding and dipole interaction through accommodating process is confirmed by pico-second order of thermal relaxation time[52,53]. Gibb's free energy of mixture defines the maximum work done in formation of it with constituents in equilibrium condition through relaxation process. Therefore, Gibb's free energy and thermal relaxation time resemble the same trend of variation with molar mass for present mixtures.

The nature of ultrasonic absorption is received to resemble characteristics of molar mass-dependent thermal relation time and Gibb's free energy (Fig. 6). The viscosity has been obtained to be the governing factor for ultrasonic absorption in the present binary liquid mixtures. An enhancement in ultrasonic absorption reveals a high ordering and significant bonding among the constituents due to exceptional hydration and the presence of physical forces through a vibrational relaxation mechanism. The analysis of ultrasonic absorption signifies that the ordering and bonding among the constituents shall be high for DCAC +PEG600 mixture due to presence of strong physical forces evinced by huge hydrogen bonding and network formation.

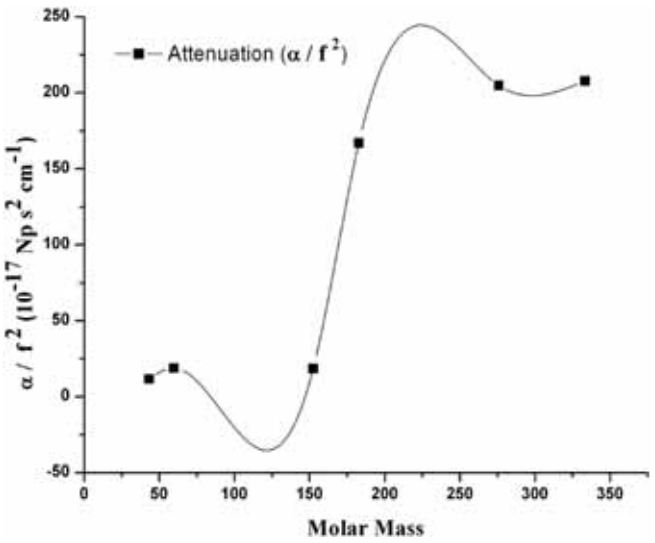

Fig. 6. Ultrasonic absorption vs. Molar mass of binary mixtures at 300K.

Conclusion

The analysis reveals that measured and estimated thermo-physical quantities for binary liquid mixtures of Dichloroacetyl chloride (DCAC) with methanol/ethanol/ carbon tetrachloride and polyethylene glycol at 300K and 100.5 kPa are justified. The deep investigation of measured and estimated parameters confirms the presence of weak intermolecular physical forces between the constituents in the present binary mixtures. The ultrasonic and related thermo-physical parameters explores that DCAC shall form a stable and strengthen binary mixture with polymers in comparison to mixture with polar and non-polar liquids. It also explores that DCAC+PEG600 mixture have significant ordering and strong bonding among the constituents in comparison to other prepared mixtures due to huge hydrogen bonding and network formation. This reveals that DCAC + PEG600 shall have low corrosiveness and high stability. The present work shall open a new dimension for the further study of hazardous chemical DCAC and shall also enhance its applicability in the form of a low corrosive binary mixture in the field of herbicides, pesticides, and fertilizers.

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Ultrasonic study of molecular interaction in binary liquid mixtures of ethyl acetate with alcohols at 303.15 K

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The ultrasonic velocity of liquids and liquid mixtures play very important role in understanding the nature of molecular interaction occurring in the system. This paper presents experimental data for density *(ρ)*, ultrasonic velocities *(u)* and viscosity values *(η)* of pure ethyl acetate, methanol, ethanol, propanol, butanol, hexanol, octanol and their binary mixtures with ethyl acetate as a common component over the whole composition range at 303.15 K. From these data acoustical parameters such as adiabatic compressibility, free volume, molar volume, available volume and their excess values are evaluated. From the properties of these acoustical parameters, the nature and strength of molecular interactions in these binary systems are discussed. The non-linear variation of these parameters shows the presence of interaction and their excess values is indicative of interaction between the components molecule in all systems.

Keywords: Ultrasonic velocity, density acoustical parameters, binary mixtures, molecular interaction.

Introduction

Present study of binary mixtures of ethyl acetate + alkanols is extension of our research work. In recent years, ultrasonic investigation of binary liquid mixtures has revolutionized the world of medical, petro chemical and pharmaceutical industries to great extent[1-5]. Ultrasonic technique has become a powerful tool for studying the molecular behavior of liquid mixtures[6-8]. This is because of its ability of characterizing physic-chemical behavior of liquid medium. Ultrasonic velocity and isentropic compressibility of liquid mixtures are useful in understanding the solute-solvent interaction[9-10] and investigation the physico-chemical behavior of liquid mixtures. Excess parameters provide valuable information about the molecular interaction and macroscopic behavior of liquid mixtures and be used to test and improve thermo dynamical models, for calculating and predicting the fluid phase equilibria[11-14]. The knowledge of excess isentropic compressibility helps in understanding the molecular orientation and study the extent of intermolecular interaction between component molecules of the liquid mixtures[15]. Fundamental thermodynamic and thermo physical properties are essential sources of information necessary for a better understanding of the non-ideal behaviour of complex systems because physical and chemical effects which are caused by molecular interactions, inter-molecular forces *etc*. of unlike molecules[16].

In recent years the ultrasonic study of properties of liquid mixtures and solvation find direct application in chemical and biochemical industry. Thermodynamic and transport properties of liquid of liquid mixtures have been extensively used to study the departure of a real liquid mixture behavior from ideality. The measurements of ultrasonic velocity, viscosity and density have been adequately employed in understanding the molecular interactions in liquid mixtures.

In order to examine molecular interactions, we report ultrasonic velocity *(u)*, density *(ρ)* and viscosity *(η)* of binary mixtures of ethyl acetate with alkanols over entire composition range at 303.15 K. The experimental value of ultrasonic velocity, density and viscosity were used to calculated excess isentropic compressibility (β_s^E), excess molar volume (V_m^E), excess free volume (V_f^E) and excess available volume (V_a^E). These parameters are quite sensitive towards the intermolecular interactions

between the component molecules in the mixtures. The dependence of these parameters on composition of the mixtures reveals the nature and extent of interaction between component molecules.

Experimental

Material : The chemicals used in the present work were high purity laboratory reagent grade samples of ethyl acetate, methanol, ethanol, propanol, butanol, hexanol, octanol purchased from Merck Chem. Ltd. India. All chemicals was stored over sodium hydroxide pellets for several days and fractionally distilled twice[17]. All chemicals was purified by the method described by Zhao *et al.*[18] ethyl acetate was dried over K_2CO_3, filtered and distilled were discarded. All the chemicals were stored in dark bottles over freshly activated molecular sieve to minimize adsorption of moisture. The purity of the solvent was ascertained by comparing the measured density, dynamic viscosities and sound velocity of the pure component at 303.15 K with the available literature[19-28] as shown in Table 1. The reported experimental values of density *(ρ)* and viscosity *(η)* conform closely to their corresponding literature values.

Measurements : Six binary system *viz.* ethyl acetate + methanol, ethyl acetate + ethanol, ethyl acetate + propanol, ethyl acetate + butanol, ethyl acetate + hexanol and ethyl acetate + octanol were studied. Each sample mixture was prepared, on mass basis, by mixing the calculated volume of liquid components in specially designed glass stoppered bottles. All binary mixtures were prepared by weight covering the entire mole fraction range. The components of binary mixtures were injected by means of syringe in to the glass vials of sealed with rubber stopper in order to check evaporation losses during sample preparation. The mass measure-ments were carried out using an single pan analytical balance with an accuracy of ± 0.00001×10^{-3} kg as described elsewhere[29]. The possible error in the mole fraction was estimated to be less than 1×10^{-4}. Five samples were prepared for one system, and their density and sound velocity were measured on the same day.

Density : Densities of pure liquids and their binary mixtures were determined by using a double-arm pycnometer 30 with a bulb of 25 cm^3 and a capillary of an internal diameter of about 1 mm is used to measure the densities *(ρ)* of pure liquids and binary mixtures. The pycnometer is calibrated by using conductivity water (having specific conductance less than 1×10^6 ohm-1) with 0.9970 and 0.9940 g cm^{-3} as its densities at T = 303.15 K, respectively. The pycnometer filled with air bubbles free liquids is kept in a thermostate water bath controlled with a thermal equilibrium. The precision of the density measurements was estimated to be ±0.0002 g cm^{-3}. The observed values of densities of pure ethyl acetate, methanol, ethanol, propanol, butanol, hexanol and octanol at 303.15K were 0.8820, 0.7840, 0.7720, 0.8070, 0.8040, 0.8128 and 0.8242 $g.m^{-3}$ which compare well with corresponding literature values of respectively.

Sound velocity : The ultrasonic velocities were measured using a multifrequency ultrasonic inter-ferometer working at 3 M.Hz. The meter was calibrated with water and benzene at 303.15 K. The measured values of ultrasonic velocities of pure ethyl acetate, methanol, ethanol, propanol, butanol, hexanol and octanol at 303.15K were 1125, 1084, 1141, 1182, 1196, 1298 and 1327 $m.s^{-1}$ respectively, which compare well with the corresponding literature values.

Viscosity : The viscosity of pure liquids and their binary mixture were measured using suspended ubbelohde type viscometer[31] having a capacity of about 15 ml and the capillary having a length of about 90 mm and 0.5 mm internal diameter has been used to measure the flow time of pure liquids and liquid mixtures and it was calibrated with triply distilled water, methanol and benzene at 303.15K. The details of the methods and techniques have been described by researchers[32]. The efflux time was measured with an electronic stop watch (Racer) with a time resolution (±0.015), and an average of at least four flow time readings was taken. Glass stopper was placed at the opening of the viscometer to prevent the loss due to evaporation during measure-ments. The two bulbs reservoir, one at the top and other at the bottom of the viscometer linked to each other by U type facilitate the free full of liquid at atmospheric pressure. Viscosity values *(η)* of pure liquids and their binary mixtures are calculated using the solution.

$$\frac{\eta}{\rho} = \text{at} - \frac{b}{t}$$

Where t is the efflux time and a and b are viscometric constants.

The measured values of viscosities of pure ethyl acetate, methanol, ethanol, propanol, butanol, hexanol and octanol at 303.15 K were 0.4402, 0.4949, 1.1399, 1.5477, 2.2045, 4.5642 and 7.8512 CP which compare well with the corresponding literature values.

Theoretical

According to Bingham[26] and Macleod[27] free volume (V_f) can be calculated from the sound velocity and viscosity by the relation given below

$$V_f = (M\,U/\,k\eta)^{3/2} \quad (1)$$

Where M is the molecular weight (gm)

U is the sound velocity (cm/sec)

η is the viscosity (poise)

k is the constant, equal to 4.28×10^9, independence of temperature and V_f, the free volume is in milliliters per mole.

The available volume (V_a) was calculated from the following expression obtained by combining the equation of Jocobson and Schaff

$$V_a = V_m\left(1-\frac{u}{u_\infty}\right) \quad (2)$$

Where V_m is the molar volume, u_1 is the ultrasonic velocity in liquid and u_∞ = 1600 m/s.

The molar volume V_m calculated from the measured values of density (ρ), molar volume (V_m) was calculated using the relation

$$V_m = \frac{(X_1M_1+X_2M_2)}{\rho} \quad (3)$$

Where X_1, X_2 and M_1, M_2 are the mole fraction and molecular weight of the component 1 and 2 respectively.

The adiabatic compressibility (β_s) calculated from the measured values of density (ρ) and sound velocity (u) was calculated using the relation

$$\beta_s = u^{-2}\rho^{-1} \quad (4)$$

Where ρ is the density of liquid.

The excess value of A^E of these thermodynamic parameters have been obtained by substracting the ideal value from the experimental value

$$A^E = A_{exp.} - (X_1A_1 + X_2A_2) \quad (5)$$

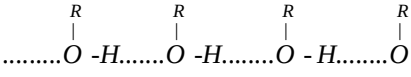
Where A represents the parameter such as intermolecular free length, molar volume, available volume, free volume and isentropic compressibility and X_1 and X_2 are the mole fractions of components whose parameters.

Results and Discussion

The experimental determined values of density (ρ), ultrasonic velocity (u) and viscosity (η) of all the pure liquids at 303.15 K are presented in Table 1 and the same for the six binary systems are liquid in Table 2. The excess values of isentropic compressibility (β_s^E), molar volume (V_m^E), free volume (V_f^E) and available volume (V_a^E) at the 303.15 K are reported in Table 3.

Alkanols are liquids which are associated through the hydrogen bonding and in the pure state, they exhibit an equilibrium between the monomer and multimer species. Also, they can be associated with any other group having some degree of polar attraction[33]. Due to polar nature of ethyl acetate and alkanols, the dipole-dipole interaction prevail in these mixtures. When the compounds are mixed the changes the occur in association equilibria are evidently repture of the hydrogen bonds in pure ethyl acetate and alkanols, dipole-dipole interactions and the formation of O – H----O hydrogen bonds between the components.

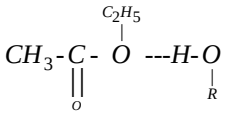
The 1-alkanols are associated through hydrogen bonding.



and ethyl acetate- 1-alkanols interactions are due to hydrogen bonding between the oxygen atom of the ethyl acetate and the proton of hydrogen group of alkanols.

Table 1 – Physical properties of pure components at 303.15 K.

Component	Density (ρ) g-m^{-3}		Ultrasonic Velocities (u) m.s^{-1}		Viscosity (η) CP	
	Observed	Literature	Observed	Literature	Observed	Literature
Ethyl acetate	0.8820	0.8885[20]	1125	1115.0[16]	0.4402	0.4000 [23]
Methanol	0.7840	0.7817 [20]	1084	1084.0 [27]	0.4949	0.5040 [21]
Ethanol	0.7720	0.7807 [19]	1141	1144.3 [21]	1.1399	1.3560 [19]
Propanol	0.8070	0.8003 [26]	1182	1182.6 [21]	1.5477	1.6626 [21]
Butanol	0.8040	0.8020 [21]	1196	1196.6 [21]	2.2045	2.2740 [22]
Hexanol	0.8128	0.8118 [21]	1298	1282.0 [28]	4.5642	4.5930 [24]
Octanol	0.8242	0.8187 [25]	1327	1330.8 [25]	7.8512	7.6630 [24]



The result present in Table 2, show non-linear behaviour of isentropic compressibility, molar volume , free volume and available volume which is further substantial by their excess values (Table 3). All the seven organic compounds namely ethyl acetate, methanol, ethanol, propanol, butanol, hexanol and octanol are a polar organic compounds having dipole moment 1.78 D, 1.70 D, 1.69 D, 1.68 D, 1.66 D, 1.60 D and 1.68 D respectively. Normally more the dipole moment, stronger is the intermolecular attraction, which results in decreasing of free space between molecules and increase in the ultrasonic velocity.

The values of excess isentropic compressibility (β_s^E) are negative over the entire range of concentration in all the six binary system at 303.15 K. The value of excess isentropic compressibility (β_s^E) are plotted against the mole fraction of ethyl acetate and are shown in Figure 1.

Table 2 – Values of density, ultrasonic velocity, isentropic compressibility, molar volume, available volume and free volume properties for binary liquids mixtures of ethyl acetate + methanol, ethyl acetate + ethanol, ethyl acetate + propanol, ethyl acetate + butanol, ethyl acetate + hexanol and ethyl acetate + octanol at 303.15 K.

X_1	ρ k.gm^{-3}	u m/s	$\beta_s\times10^{-8}$ (m^{2}N^{-1})	$V_m\times10^6$ m^{3}mol^{-1}	$V_a\times10^6$ m^{3}mol^{-1}	$V_f\times10^6$ m^{3}mol^{-1}
			Ethyl acetate + Methanol			
0.0000	784.0	1084	108.54	40.8673	13.179	0.06639
0.1039	796.8	1099	100.39	47.5245	14.881	0.08953
0.2248	819.2	1103	100.33	54.4992	16.928	0.11699
0.3129	839.5	1105	96.54	59.0643	18.273	0.13807
0.4370	848.3	1110	95.67	66.6542	20.412	0.17316
0.5474	867.5	1114	92.88	72.3090	21.963	0.20581
0.6409	870.9	1117	92.02	78.0508	23.561	0.23810
0.7128	879.0	1118	91.01	81.9179	24.677	0.26139
0.8164	879.2	1122	90.34	88.5081	26.441	0.30139
0.9104	880.5	1123	90.05	94.3665	28.133	0.33654
1.0000	882.0	1125	89.58	99.8979	29.657	0.38161
			Ethyl acetate+ Ethanol			
0.0000	772.0	1141	99.49	59.6761	17.119	0.03536
0.1049	802.5	1137	96.38	62.9054	18.203	0.09237
0.2090	815.7	1135	95.16	67.2489	19.544	0.11781
0.3105	827.8	1134	93.93	71.4184	20.800	0.15538
0.4166	839.2	1133	92.81	75.7609	22.112	0.17907
0.5094	849.6	1132	91.84	79.4294	23.233	0.20957
0.6076	860.4	1131	90.85	83.2250	24.395	0.25199
0.7150	863.9	1130	90.65	88.1223	25.885	0.28264
0.8069	877.6	1128	89.54	91.1441	26.887	0.32369
0.9030	882.7	1126	89.35	95.1972	28.202	0.34887
1.0000	882.0	1125	89.58	99.8979	29.657	0.38161
			Ethyl acetate + Propanol			
0.0000	807.0	1182	88.68	74.4563	19.451	0.03511
0.1074	813.3	1173	89.35	77.5792	20.703	0.06146
0.2086	826.2	1169	88.56	79.7993	21.495	0.09824
0.3145	832.1	1161	89.15	82.8013	22.718	0.13382
0.4099	842.8	1159	88.33	84.9257	23.407	0.17883
0.4758	850.9	1154	88.24	86.2868	24.052	0.20368
0.54307	860.9	1150	87.82	87.4748	24.602	0.25201
0.6127	864.7	1142	88.67	89.3453	25.575	0.27686

0.7564	868.5	1138	88.90	93.5897	27.024	0.32271
0.9126	878.8	1134	88.48	97.4750	28.399	0.35690
1.0000	882.0	1125	89.58	99.8979	29.657	0.38161
			Ethyl acetate + Butanol			
0.0000	804.0	1196	86.95	92.1902	23.780	0.02879
0.1063	805.6	1194	87.06	93.8435	23.812	0.05784
0.2151	816.8	1184	87.33	94.4294	24.551	0.09105
0.3213	826.9	1180	86.85	95.0707	24.956	0.13714
0.4327	832.2	1176	86.88	96.3355	25.528	0.14106
0.5192	842.0	1170	86.75	96.6507	25.974	0.22702
0.6266	842.4	1167	87.16	98.3882	26.626	0.27918
0.7124	858.1	1154	87.50	97.9889	27.314	0.31567
0.8127	866.6	1142	88.47	98.6404	28.235	0.34790
0.9044	874.2	1134	88.94	99.2555	28.908	0.36108
1.0000	882.0	1125	89.58	99.8979	29.657	0.38161
			Ethyl acetate + Hexanol			
0.0000	812.8	1298	73.02	125.6914	23.724	0.01768
0.0996	821.4	1292	72.92	122.6634	23.612	0.03523
0.2225	833.8	1287	72.40	118.7742	23.235	0.05597
0.3149	835.5	1275	73.62	116.9760	23.760	0.08122
0.4151	840.6	1257	75.29	114.5933	24.565	0.11401
0.5186	846.6	1247	75.95	112.0864	24.729	0.15624
0.6083	854.4	1240	76.11	109.5595	24.948	0.19927
0.7096	861.7	1222	77.70	106.9770	25.273	0.24487
0.8066	867.2	1210	78.75	104.7255	25.526	0.28991
0.9041	878.0	1192	80.15	101.8771	25.978	0.33007
1.0000	882.0	1125	89.58	99.8979	29.657	0.38161
			Ethyl acetate + Octanol			
0.0000	824.2	1327	68.89	158.0052	26.959	0.01165
0.1056	825.9	1312	70.33	152.2800	27.410	0.02292
0.2095	830.0	1294	71.94	146.2509	27.970	0.03838
0.3174	831.8	1275	73.94	140.4730	28.533	0.06206
0.4286	838.7	1239	77.66	133.7374	30.174	0.09634
0.5083	840.0	1225	79.32	129.5386	30.360	0.11928
0.6196	844.4	1214	80.35	123.3172	31.750	0.17562
0.7090	858.6	1192	81.96	145.9131	31.958	0.17723
0.8064	865.1	1164	85.31	111.2675	32.126	0.27175
0.9044	871.6	1148	87.05	105.7013	33.254	0.29587
1.0000	882.0	1125	89.58	99.89795	29.657	0.38161

The sign of excess isentropic compressibility play a vital role in assessing the compactness due to molecular interaction in liquid mixtures through charge transfer, dipole-dipole interaction and dipole induced dipole interactions interstitial accommodation and orientation ordering leading to more compact structure making, which enhances excess isentropic compressibility to have negative values. Fort and Moore[34] suggested that the liquid having different molecular size and shape mix well there by reducing the volume which causes the values of β_S^E to be negative. It is also suggested that liquids are less compressible when compared to their ideal mixtures signifying the chemical effects including charge transfer forces, formation of hydrogen bond and other complex forming interactions. It can also be said that the molecular interaction are strong in these binary liquid mixtures and that the medium is highly packed. Similar results were obtained by earlier worker[35]. The negative value of β_S^E in these mixtures can be associated with a structure forming tendency.

Table 3 – Excess values of isentropic compressibility (β_s^E), molar volume (V_m^E), available volume (V_a^E) and free volume (V_f^E) properties for binary liquids mixtures of ethyl acetate + methanol, ethyl acetate + ethanol, ethyl acetate + propanol, ethyl acetate + butanol, ethyl acetate + hexanol and ethyl acetate + octanol at 303.15 K.

X_1	β_s^E×10–7 (m^2N^{-1})	V_m^E×10^6 m^3mol^{-1}	V_a^E × m^3mol^{-1}	V_f^E ×10^6 m^3mol^{-1}
		Ethyl acetate + Methanol		
0.0000	0.00	0.00000	0.000	0.0000
0.1039	-61.8	-0.52201	-0.011	-0.0096
0.2248	-39.4	-0.66072	-0.247	-0.0202
0.3129	-60.6	-0.77383	-0.262	-0.0269
0.4370	-45.8	-0.80962	-0.283	-0.0309
0.5474	-52.8	-0.87129	-0.305	-0.0331
0.6409	-43.6	-0.95002	-0.337	-0.0303
0.7128	-40.1	-0.62853	-0.384	-0.0297
0.8164	-27.1	-0.55257	-0.312	-0.0223
0.9104	-12.2	-0.54600	-0.223	-0.0168
1.0000	0.00	0.00000	0.000	0.0000
		Ethyl acetate+ Ethanol		
0.0000	0.00	0.00000	0.000	0.0000
0.1049	-20.6	-0.99258	-0.232	-0.0206
0.2090	-22.6	-1.83336	-0.252	-0.0257
0.3105	-24.8	-1.94880	-0.268	-0.0312
0.4166	-25.4	-2.67661	-0.270	-0.0389
0.5094	-25.9	-2.73675	-0.273	-0.0412
0.6076	-26.2	-2.88955	-0.342	-0.0495
0.7150	-17.5	-1.31421	-0.349	-0.0325
0.8069	-19.4	-0.99000	-0.238	-0.0246
0.9030	-11.9	-0.79942	-0.197	-0.0211
1.0000	0.00	0.00000	0.000	0.0000
		Ethyl acetate + Propanol		
0.0000	0.00	0.00000	0.000	0.0000
0.1074	-5.75	-0.39267	-0.155	-0.0108
0.2086	-3.10	-0.43678	-0.185	-0.0191
0.3145	-4.85	-0.64416	-0.225	-0.0216
0.4099	-7.22	-0.84248	-0.227	-0.0369
0.4758	-8.65	-0.97433	-0.391	-0.0486
0.5430	-13.4	-1.80306	-0.412	-0.0512
0.6127	-5.62	-0.69878	-0.312	-0.0416
0.7564	-4.57	-0.41016	-0.213	-0.0315
0.9126	-3.16	-0.19909	-0.130	-0.0186
1.0000	0.00	0.00000	0.000	0.0000
		Ethyl acetate + Butanol		
0.0000	0.00	0.00000	0.000	0.0000
0.1063	-1.69	-0.83451	-0.143	-0.0084
0.2151	-1.84	-0.98179	-0.198	-0.0134
0.3213	-9.46	-1.38436	-0.371	-0.0150
0.4327	-12.0	-1.81050	-0.509	-0.0404
0.5192	-15.6	-2.45928	-0.615	-0.0450
0.6266	-14.3	-1.36900	-0.648	-0.0512
0.7124	-13.1	-1.30851	-0.508	-0.0355
0.8127	-6.17	-0.88668	-0.226	-0.0131
0.9044	-3.81	-0.79466	-0.139	-0.0108
1.0000	0.00	0.00000	0.000	0.0000
		Ethyl acetate + Hexanol		
0.0000	0.00	0.00000	0.000	0.0000
0.0996	-17.4	-0.45637	-0.702	-0.0187
0.2225	-43.0	-1.17608	-1.809	-0.0426
0.3149	-46.1	-1.59146	-1.831	-0.0516
0.4151	-46.0	-1.88840	-1.925	-0.0547
0.5186	-56.5	-2.25452	-2.071	-0.0398
0.6083	-69.8	-1.43844	-2.684	-0.0310
0.7096	-60.6	-1.40800	-2.982	-0.0213
0.8066	-56.2	-0.75911	-1.621	-0.0166
0.9041	-38.4	-0.49263	-0.946	-0.0120
1.0000	0.00	0.00000	0.000	0.0000
		Ethyl acetate + Octanol		
0.0000	0.00	0.00000	0.000	0.0000
0.1056	-7.43	-0.42861	-0.166	-0.0278
0.2095	-12.8	-0.43692	-0.445	-0.0508
0.3174	-15.1	-0.92541	-0.717	-0.0670
0.4286	-16.97	-1.04906	-2.058	-0.0738
0.5083	-10.81	-1.07905	-2.090	-0.0804
0.6196	-9.50	-1.32444	-3.126	-0.0967
0.7090	-8.90	-0.85666	-3.864	-0.0652
0.8064	-7.65	-0.72863	-2.126	-0.0503
0.9044	-5.53	-0.25366	-1.101	0.0315

A perusal of Table 3 also reveal that the values of excess free volume (V_f^E) are negative with the increase in concentration of ethyl acetate (X_1). The value of excess

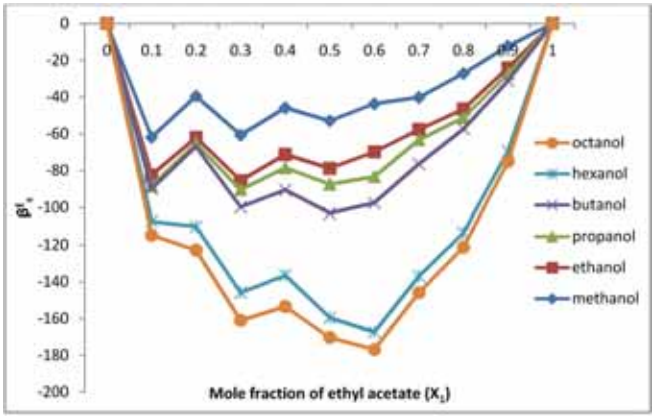


Fig. 1. Plots of excess isentropic compressibility β_s^E versus mole fraction of ethyl acetate (X_1) at 303.15 K for binary mixtures of ethyl acetate with methanol, ethanol, propanol, butanol, hexanol and octanol at 303.15 K.

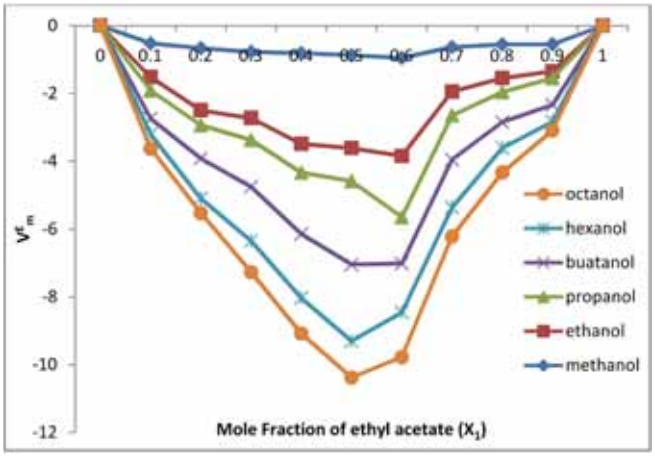


Fig. 2. Plots of excess molar volume (V_m^E) versus mole fraction of ethyl acetate (X_1) at 303.15 K for binary mixtures of ethyl acetate with methanol, ethanol propanol, butanol, hexanol and octanol at 303.15 K.

free volume V_f^E plotted against the mole fraction of ethyl acetate (X_1) and are shown in Figure 3. The observed value of (V_f^E) over whole range of composition suggest the weak interaction involving dispersion forces between the component molecules. Similar results have also been found in other binary liquid mixture[36].

It is evident from Table 3 that the value of excess available volume (V_a^E) are negative for all six binary liquid system at 303.15 K. The value of V_a^E plotted against the mole fraction of ethyl acetate and shown Figure 4. Similar results were also obtained by prakash *et al.*[37] for binary mixtures of ketones. The depolymerisation of hydrogen bonded alcohols

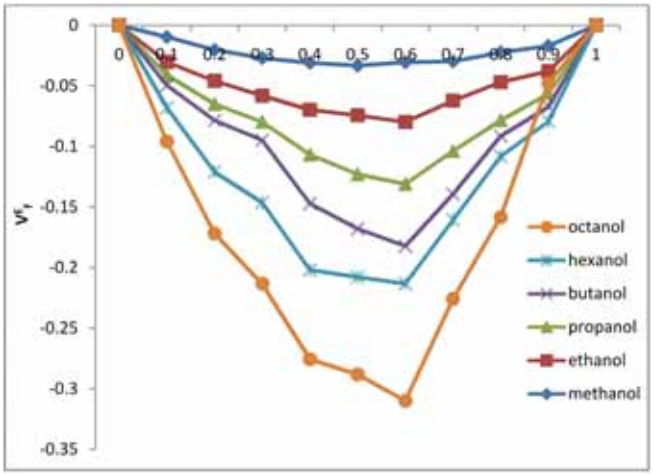


Fig. 3. Plots of excess free volume V_f^E versus mole fraction of ethyl acetate (X_1) at 303.15 K for binary mixtures of ethyl acetate with methanol, ethanol, propanol, butanol, hexanol and octanol at 303.15 K.

aggregates and decrease in dipolar association of component molecules leads to expansion of volume dominating interstitial accommodation which causes value of excess available volume (V_a^E) but it is compensated by charge transfer complex formation between hydrogen of alcohols and oxygen of ethyl acetate.

The charge in molar volume, free volume and available volume with change in composition in these systems, indicate the variations in cohesive forces of these system[38]. A perusal of the sign and magnitude of the excess values of the parameters (β_s^E), (V_m^E), (V_a^E) and (V_f^E) show that the strength of the molecular interaction

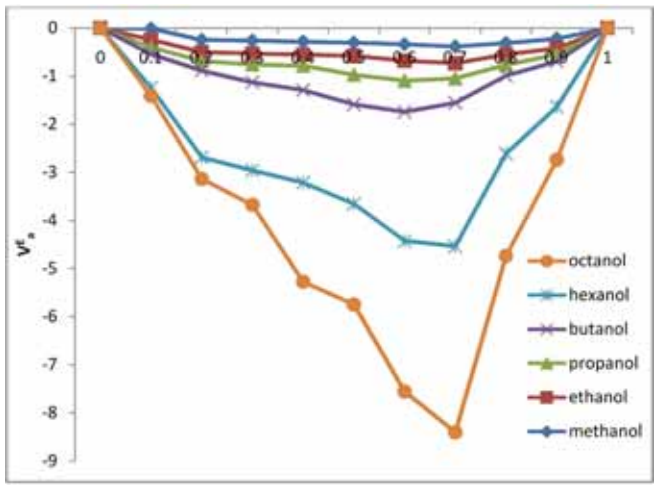
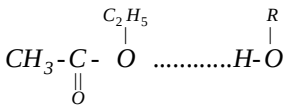


Fig. 4. Plots of excess available volume (V_a^E) versus mole fraction of ethyl acetate (X_1) at 303.15 K for binary mixtures of ethyl acetate with methanol, ethanol propanol, butanol, hexanol and octanol at 303.15 K.

between the component molecules. The present study point at clearly that in all six binary systems ethyl acetate is involved in the charge transfer interaction with alcohols. The oxygen atom of ethyl acetate being strongly electronegative would have tendency to attract electropositive hydrogen of alcohols resulting in the formation of new species, showing the negative value of excess thermodynamic properties.

The negative deviations of high magnitude lead to the unstable complex formation between the hetero molecules of the mixtures. In the present study the negative excess volume indicates the breaking of hydrogen bond of alcohols polymers as alcohol is diluted with ethyl acetate and association between unlike molecules causing contraction with increasing concentration of ethyl acetate. Therefore it can be

concluded that AB type strong specific interaction take place leading to a bonding like (– H---O –) Which results in the formation of a complex of the type



The results reveal that the intermolecular interaction decreases with the increasing size of the alcohol molecules[39]. Hydrogen bonding strength also decreases with decreasing dipole moment of the alcohol molecules.

Conclusion

In this paper, an attempt is made to measure densities *(ρ)*, ultrasonic velocity *(u)* and Viscosity *(η)* at 303.15 K over the entire range of mixture composition of ethyl acetate with methanol, ethanol, propanol, butanol, hexanol and octanol out of these measured data, excess isentropic compressibility (β_s^E), excess molar volume (V_m^E), excess free volume (V_f^E) and excess available volume (V_a^E) have been calculated.

The negative deviations are observed in the case of excess isentropic compressibility (β_s^E), excess molar volume (V_m^E), excess free volume (V_f^E) and excess available volume (V_a^E) are observed for all binary mixtures of ethyl acetate with methanol, ethanol, propanol, butanol, hexanol, octanol. The results are analyzed in the sight of molecular interactions between the components. It may be concluded that the interaction resulting in the interstitial accommodation of ethyl acetate in to 1-alkanols are the predominant factor over dipole-dipole interaction.

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Periodicity dependent properties of holey phononic crystals

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Phononic crystals, which are structures with periodicities on the scale of the incident sonic wavelength, are of much interest due to the potential for new properties, such as band gaps and high-efficiency transmission. The phononic properties of holey structures have been particularly studied because of their ease of fabrication and scalability. Recently our group has demonstrated super resolution imaging using structured holey lenses. However, the resolution capacity of phonic crystals having a periodic arrangement of regular holes is limited by the Wood anomaly, at which some of the wave field components vanish from the transmission spectrum. This paper discusses an alternative approach to overcome the Wood anomaly, using aperiodic lenses. We show deep subwavelength imaging ($\lambda/32$) of a surface notch in a mild steel sample using the proposed unstructured phononic holey lens.

Keywords: Periodicity, phononic crystal, super resolution, unstructured phononic lens, wood anomaly.

Introduction

Phononic crystals are the structures with periodicities on the scale of the incident sonic wavelength. They have attracted considerable attention due to the potential for new properties, including the possibility of overcoming the diffraction limit[1-2], effective sound transmission[3-7] and frequency filtering[8-9]. Recently, phononic properties of periodic porous structures have been of research interest because of ease of fabrication and potential for Non-destructive evaluation and non-invasive medical diagnostics. Other applications such 'metal foams', include acoustic damping and deep sub-wavelength imaging[10-13]. However, periodicity induced bandgaps at certain frequencies, a phenomenon known as the 'Wood anomaly' are an important limitation of such approaches, limiting the resolution achievable in practice[14-15]. This paper, discusses aperiodic phononic crystals as an alternative route to overcome the Wood anomaly. Using aperiodic lenses, we demonstrate, deep sub-wavelength imaging of a canonical surface notch defect down to 1/32 of the operating wavelength (λ) in the ultrasonic regime.

This paper is organized as follows, firstly an introduction to the periodicity dependent transmission characteristics of phononic crystals is given. The phenomenon of, Wood anomaly is then presented followed by a possible solution to overcome this limitation. The

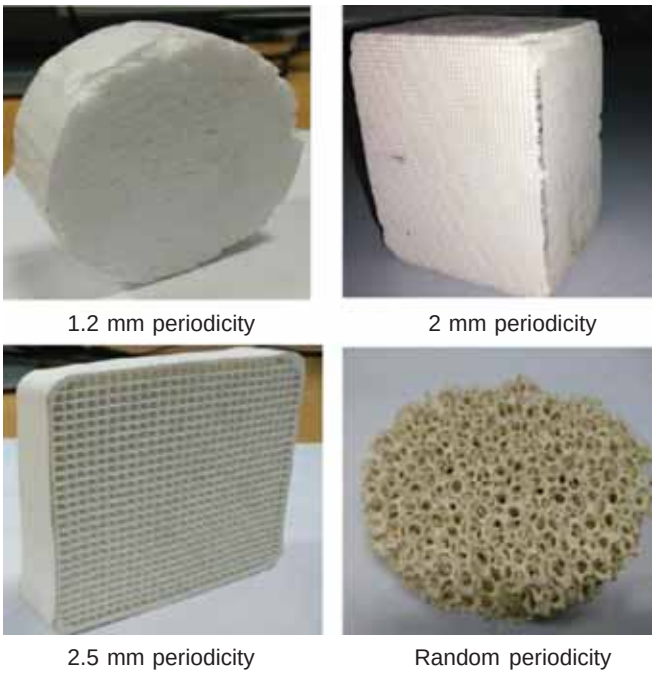

Fig. 1. Photographs of phononic crystals with different periodicity values, as indicated.

potential application of wavelength imaging is then discussed. Finally results showing deep sub-wavelength imaging of a surface notch in a metallic sample are presented and discussed. The paper concludes with an outlook for further work.

To study the transmission characteristics of phononic crystals, we considered 4 different embodiments having periodicity values of 1.2 mm, 2 mm, 2.5 mm an aperiodic porous foam, as shown in Figure 1. The porous phononic crystal contains random hole sizes (2-10 mm range, as determined from X-ray tomograms), arranged randomly.

Experimental procedure

Immersion ultrasonic scan in the through-transmission mode was utilized for the experiments. An illustration of the experimental set-up is shown in Figure 2(b). A commercial piezoelectric transducer (Panametrics NDT, https://www.olympus-ims.com/en/ultrasonic-transducers/) with a central frequency of 500 kHz is used for the excitation, applied as a 3 cycle Hanning windowed tone-burst signal provided through the RITEC 4000 Pulser-Receiver (Ritec Inc., http://www.ritecinc.com/, Warwick, USA). The phononic crystal was immersed in water, placed perpendicularly in front of the transducer, as shown in Figure 2. The wave fields transmitted across the sample and received past the phononic crystals were monitored using a Polytec Laser Doppler Vibrometer (LDV), consisting of an independent OFV-130 optical scanning sensor head and an OFV-551 controller (http://www.vibrometry.co.kr/OFV-552.pdf). The output from the controller is fed to an oscilloscope. A thin retroreflective tape was attached to the surface of phononic crystal at the spot illuminated by the laser point so as to enhance the optical back-scattering from the laser beam. The experiments are repeated for different phononic crystals having different periods. The Transmission ratio (TR or spectral ratio, is the ratio of the spectrum with phononic crystal to without phononic crystal) is calculated for each of the cases (see: Amireddy *et al.*, APL 2016, *Sci. Rep.* 2017, APL 2018 for details on experiments and procedure to calculate TR). Following this, the same experimental procedure was followed for imaging of a deep sub-wavelength ($\lambda/32$) surface notch in a mild steel sample.

The experimental configuration is shown in Figure 2.

Results and Discussion

After completion of the A-Scans (on time trace) 'without' and 'with' the phononic crystal, the Transmission Ratio was calculated for different periodicity cases. The corresponding TR variation with the frequency for the different phononic crystals is shown

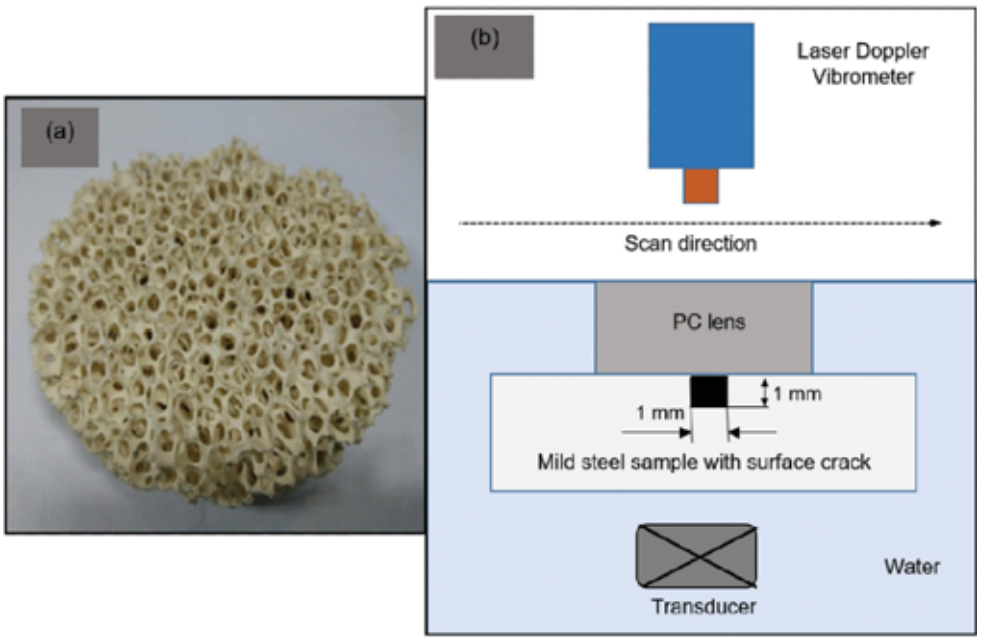

Fig. 2. (a) Photograph of the phononic crystal used to image the deep sub-wavelength surface notch in the mild steel sample; (b) Illustration of the experimental set-up used to obtain the TR of different phononic crystals and imaging of defects in mild steel sample.

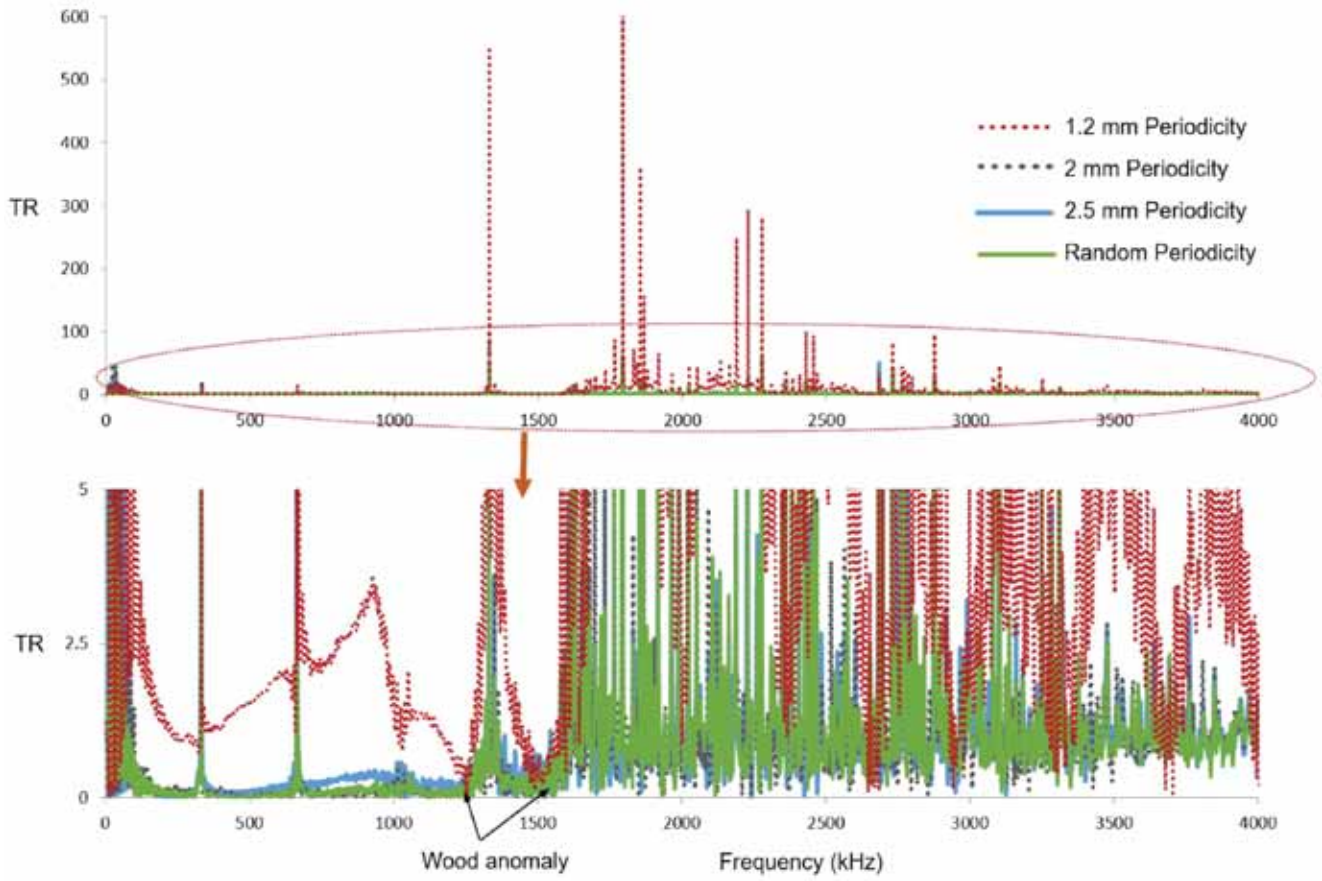

Fig. 3. Experimental results showing the transmission ratio (TR) for phononic crystals with different periodicity values indicated in Figure 1 - the zoomed-in figure shows the locations of the Wood anomaly more clearly.

in figure 3. From the results, it is clear that the TR values are varying for different phononic crystals and are dependent on the periodicity. It is also observed that, there are bandgaps (zero transmission at certain frequencies) or Wood anomalies in the transmission spectrum of periodic phononic crystals. The Wood anomaly is a common problem of periodic phononic crystals and it limits the transmission characteristics, thereby limiting the resolution achievable by such meta-lenses.

To overcome the common problem (Wood anomaly) here we propose that an aperiodic phononic crystal could be an ideal candidate. The potential application of the aperiodic phononic crystal to overcome the natural diffraction limit is demonstrated by a deep sub-wave length ($\lambda/32$) imaging application. For this case, a mild steel sample with a surface through-notch (as an example of a typical canonical defect encountered in NDE applications) of length 1 mm (which is about $\lambda/32$ at the frequency studied) is considered as the object for ultrasonic imaging.

The C-scan[16] images of the sample are obtained using immersion ultrasonic testing in through-transmission mode. The experiment was performed 'without' and 'with' the porous phononic lens, and the corresponding results are shown in Figure 4. The deep sub-wavelength ($\lambda/32$) surface notch shows up well when using the porous phononic crystal as a lens.

Conclusion

This paper discussed periodicity-dependent transmission properties of phononic crystals, with attention to the problem of Wood anomaly. Experimental results demonstrating the application of the aperiodic crystals as lenses that overcome the Wood anomaly, thereby achieving deep sub-wavelength ultrasonic imaging, were presented. The aperiodic phononic crystal improves the resolution of imaging down to a feature size of $\lambda/32$ (where λ is the operating wavelength), which is the highest resolution demonstrated experimentally in the ultrasonic regime worldwide.

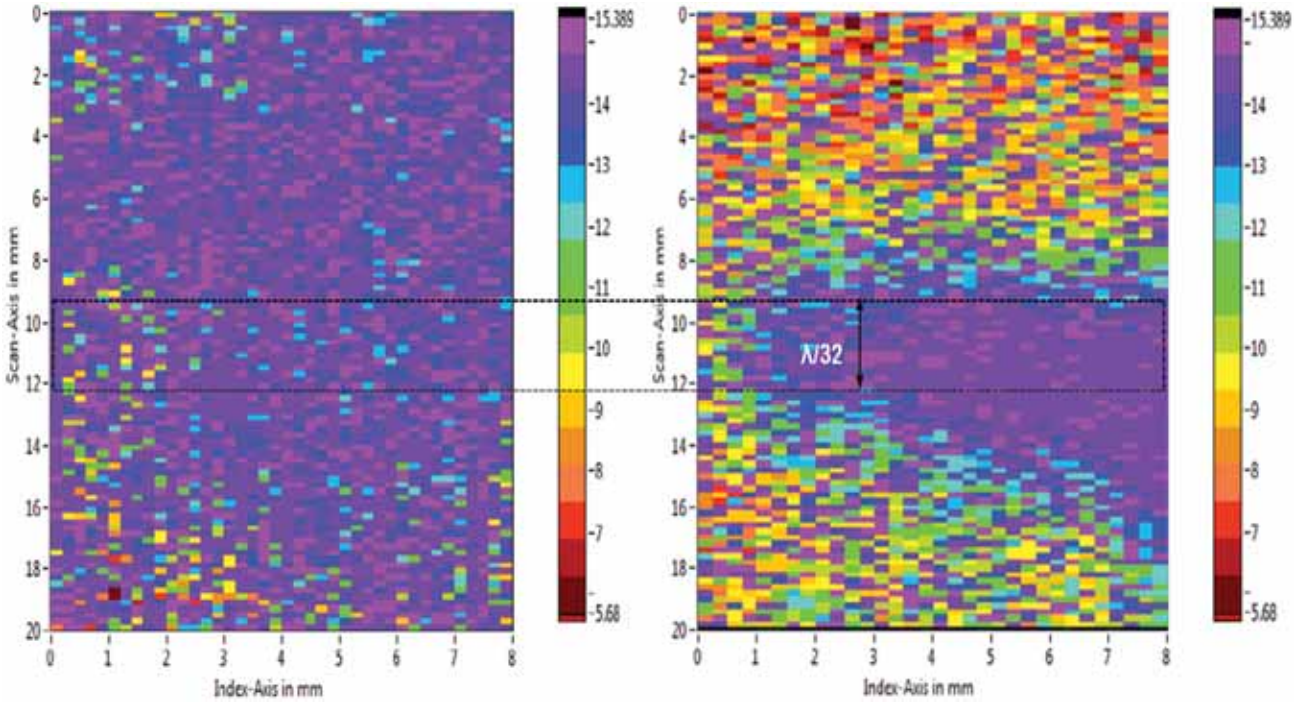

Fig. 4. Experimental C-scan images showing the deep sub-wavelength surface notch in the mild steel sample, 'without, and 'with' phononic crystal (the black colored rectangular box indicates the actual position of the notch in the mild steel sample).

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The phononic crystals used as lenses in the experiments were made out of Alumina using selective laser sintering process at ARCI, Hyderabad, India; http://www.arci.res.in/.

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Ph.D. Thesis Summary

Development of Non-contact Ultrasonic Guided Wave-based Methodology for Inspection of Steam Generator Tubes of PFBR

(Ph.D. degree was awarded to Dr. M.M. Narayanan, Scientific Officer 'E', NDE Division, under Dr. Anish Kumar, Head NDE Division, IGCAR, Kalpakkam)

The primary aim of the dissertation was to develop a rapid and non-contact ultrasonic guided wave technique and methodology for the inspection of steam generator (SG) tubes of the Prototype Fast Breeder Reactor (PFBR). The SGs of PFBR are 23.0 m long and have accessibility for NDE based-inspection only from inner sides of the tubes. As the SGs of PFBR are closed structures with accessibility for inspection only from the ID side, and are ferromagnetic, the magnetostriction property of the material was used to generate guided waves and detect defects from inner sides (12.6 mm diameter) of the SG tubes without the use of a couplant. A novel in-bore magnetostrictive transducer of 10 mm diameter was developed and successfully tested in mockup SG tubes The approaches leading to the development of the ultrasonic guided wave methodology, in-bore magnetostrictive transducer and its successful application in mockup SG tubes are discussed.

A longitudinal guided wave mode (L(0,2) mode) was optimized in the frequency range of 250-350 kHz in the light of the fastest group velocity (5380 m/s), long-range propagation of 46 m length of an SG tube, negligible dispersion, low attenuation and detection of multiple circumferential, axial, pinhole, tapered and sodium impingement defects lying in the same line in straight and bent SG tubes. Experimentally, L(0,2) mode at the optimized frequency was excited in an SG tube segment by coupling an ultrasonic transducer of the optimized frequency to the end of the SG tube. Further, to understand the wave-defect interaction and detection possibility, FE models were developed in ABAQUS to include the above-said defects in line. The FE results indicated a good detection possibility and mode conversion of L(0,2) mode to flexural modes for non-axisymmetric defects.

The transducer comprised of a permanent magnet to provide a static bias (~0.82 T) and a pair of transmitter and receiver coils wound on the permanent magnet for generating dynamic magnetic fields. Systematic 2D- axi-symmetric FE simulations were performed in FE simulation software COMSOL to model magnetostriction by coupling magnetic and elastic equations and to optimize the diameter and length of the magnet and the length of the transmitter and receiver coils. The optimized diameter and length of the magnet were 10 mm and 100 mm, respectively and the optimized length of the transmitter and receiver coils was half the wavelength (=10 mm) of L(0,2) mode at the frequency of 300 kHz. The number of turns was optimized to be 80 turns by using the

Trial studies were conducted on the SG tubes welded to the tubesheet of the mock SG test facility using the developed in-bore magnetostrictive transducer. The SG tubes have thermal expansion bends with multiple full and half circumferential grooves as reference defects. The experimental signals were denoised using the Discrete wavelet transform (DWT) and the cross-correlation technique. The signals de-noised using DWT clearly showed that multiple half and full circumferential grooves were detected with the SNR of approx. 5-10 dB. The detection sensitivity obtained was a 20%WT (0.46 mm) deep and 1 mm wide half circumferential groove based on 6 dB criterion. The spigot-tubesheet transitions were found to provide 10% reflection of the incident energy and L(0,2) mode underwent mode conversion to longitudinal, shear and Rayleigh waves in the tubesheet. Thicker tubesheets were found to be better from the perspective of inspection. Based on the analysis, two inspection locations for the actual testing of PFBR SG tubes have been chosen for the placement of the in-bore magnetostrictive transducer and they are 190 mm and 1270 mm from the top of the tubesheet.

Ph.D. Thesis Summary

Analysis and Classification of Breast Anomalies using Ultrasonic Images

(Ph.D. degree was awarded to Dr. Kriti under Ravindra Aggarwal, EIED, Thapar Institute of Engineering, Patiala)

The present research work has been carried out with an aim to enhance the diagnostic potential of B-mode ultrasound imaging modality for the diagnosis of breast abnormalities. To achieve this objective exhaustive experiments have been carried out in the present research work to (a) analyse the effect of despeckle filtering algorithms on breast ultrasound images, (b) analyse the effect of despeckle filtering algorithms on segmentation of breast tumors, (c) analyse the effect of despeckle filtering algorithms on classification of breast tumors, (d) design an efficient local binary pattern (LBP) based CAD system for classification of breast tumors, (e) design an efficient convolutional neural network based CAD system for classification of breast tumors. For carrying out the experiments a comprehensive dataset of 100 B-mode breast ultrasound images comprising of cysts, fibroadenomas, lipomas in benign category, ductal and lobular carcinomas in malignant category has been taken from a standard benchmark database, ultrasound cases.

Effect of despeckle filtering algorithms on segmentation of breast tumors- The original images as well as the images despeckled by the 06 best performing despeckling filtering algorithms have been subjected to the Chan and Vese active contour method for segmentation of breast tumors. The objective assessment of the segmentation algorithm has been carried out by computing the Jaccard index and subjective assessment has been carried out by the experienced participating radiologist. Based on the results of the study the DPAD has been selected as an optimal despeckle filtering algorithm resulting in efficient segmentation of breast tumors.

Exhaustive experiments were carried out for analysing the effect of best performing despeckle filtering algorithms on classification of breast tumors- Initially four PCA-SVM based CAD systems based on (a) texture and morphological features computed from original images (b) texture and morphological features computed from despeckled images, (c) texture features computed from original images and morphological features computed from despeckled images and (d) texture features computed from despeckled images and morphological features computed from original images. It was observed that the PCA-SVM based CAD system design based on texture features computed from original images and morphological features computed from despeckled images yielded highest classification accuracy of 96.0 % with individual class accuracy values of 95.2 % and 96.6 % respectively.

Four LBP based CAD system designs were implemented using classifiers namely, PCASVM, ANFC-LH, GA-SVM and SAE-SM by computing LBP based features computed from original images and morphological features computed from despeckled images- It was observed that the LBP based CAD system with ANFC-LH classifier yielded the highest accuracy of 96.0 % with individual class accuracy values of 90.4 % and 100 % for benign and malignant classes, respectively.

Further to compare the performance of the existing conventional approaches with the state of the art deep learning techniques- Initially four different transfer learning based CNN models with GoogleNet, VGG-19, ResNet-18 and SqueezeNet architecture have been implemented. It was observed that CNN based model based on GoogLeNet architecture yielded highest accuracy. Accordingly an optimal CNN based CAD system design based on deep feature extraction by GoogLeNet architecture and classification by ANFC-LH was designed yielding highest classification accuracy of 98.0 % with ICA values of 100 % and 96.6 % for benign and malignant cases respectively.

Journal of Pure and Applied Ultrasonics

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JOURNAL OF PURE AND APPLIED ULTRASONICS welcomes contributions on all aspects of ultrasonics including ultrasonic studies in medical ultrasonics, NDT, underwater, transducers, materials & devices and any other related topic. Contributions should fall into one of the following classes.

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Illustration - The line illustrations along with captions should be clearly drawn with black Indian ink. Figures in Excel are preferred.

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