

Ultrasonics Society of India

Ultrasonics Society of India established in 1974, is engaged in the promotion of research and diffusion of knowledge concerning the field of ultrasonics and allied areas.

Patrons : Dr. V.N. Bindal
vnbindal@yahoo.co.in
Prof. E.S.R. Gopal
gopal@physics.iisc.ernet.in

Executive Council :
President Prof. Vikram Kumar
vkmr47@gmail.com

Vice-President Dr. V.R. Singh
vrsingh@yahoo.com
Prof. R.R. Yadav
rryadav1@rediffmail.com

General Secretary Dr. Yudhister Kumar Yadav
kyadav6659@gmail.com

Joint Secretary Prof. O.P. Chhankar
opchhankar28@gmail.com

Treasurer Shri G.S. Lamba
gslamba1957@gmail.com

Publication Secretary Dr. Devraj Singh
dsingh13@amity.edu

Members Dr. S.K. Jain
skjainnpl@yahoo.co.in
Dr. (Mrs.) Kirti Soni
2006.kirti@gmail.com
Dr. Ganeswar Nath
ganesw_nath99@yahoo.co.in
Dr. N.R. Pawar
pawarsir1@gmail.com
Prof. S.S. Mathur
sartajmathur@yahoo.co.in
Dr. Janardan Singh
dr_janardansingh@yahoo.com
Dr. Mukesh Chandra
mchandra1948@yahoo.in
Shri G.K. Arora
gyanarora1935@yahoo.co.in
Mrs. Vyoma Bhalla
bhallavyoma@gmail.com
Prof. Pankaj
profpankaj99@gmail.com
Dr. Krishan Lal
krish41ster@gmail.com
(Immediate Past President)

Co-opted members Dr. (Mrs.) J. Poongodi
poogodinagaraj@gmail.com
Dr. Chandra Prakash
cprakash2014@gmail.com

Special invitees Dr. S.S.K. Titus
titus@nplindia.org
Mr. Gurmukh Singh
guru6850@gmail.com

Membership of the Society is open to individuals without distinction of sex, race or nationality and to bodies who subscribe to the aims and objectives of the Society.

The membership fee is as follows :

Class of Membership	Subscription (one time)
Honorary Fellow	Nil
Life Fellow / Member	Rs 3000/-
Associate Member	Rs 1000/- (for 5 yrs.)
Corporate Member	Rs 20000/-
Life Fellow / Member (Foreign)	US \$ 150
Corporate Member (Foreign)	US \$ 1000

Membership forms and the relevant information can be downloaded from the website or obtained from :

The General Secretary, Ultrasonics Society of India
CSIR-NPL, Dr. K.S. Krishnan Marg, New Delhi-110012
E-mail : ykyadav@nplindia.org

A Quarterly Publication of Ultrasonics Society of India

Journal of Pure and Applied *Ultrasonics*

No. 1	Volume 39	January-March 2017
-------	-----------	--------------------

Chief Editor : Prof. S.K. Jain
The NorthCap University, Gurgaon
Former Chief Scientist – CSIR-NPL
skjainnpl@yahoo.co.in

Editorial Board :
Prof. S.S. Mathur Formerly Prof., Indian Institute of Technology, New Delhi
sartajmathur@yahoo.co.in

Dr. P. Palanichamy Formerly Scientist, IGCAR, Kalapakkam, Tamil Nadu
ppc9854@gmail.com

Prof. R.R. Yadav Professor, Allahabad University, Allahabad, Uttar Pradesh
rryadav1@rediffmail.com

Publication Committee :

Dr. Devraj Singh Amity School of Engineering & Technology, New Delhi
Prof. Pankaj Dayalbagh Educational Institute, Agra
Dr. Sanjay Yadav CSIR-National Physical Laboratory, New Delhi
Dr. Y. K. Yadav CSIR-National Physical Laboratory, New Delhi
Dr. Kirti Soni CSIR-National Physical Laboratory, New Delhi
Mrs. Vyoma Bhalla Amity School of Engineering & Technology, New Delhi
Shri G. S. Lamba CSIR-National Physical Laboratory, New Delhi
Dr. J. Poongodi Kamraj College, Thoothukudi, Tamil Nadu
Shri Gurmukh Singh Formerly Deputy Director, ERTL (North), New Delhi

SUBSCRIPTION (postage paid)

Single	Rs. 750/-	US\$ 60/-
Annual	Rs. 3000/-	US\$ 250/-
USI members	Free	

ADVERTISEMENT

The Journal offers opportunity of wide and effective publicity for the manufacturer, suppliers of ultrasonic equipment, device and materials and also for scientific instruments and components. Tariff is as follows :

Back Cover	Rs. 5000/-	US \$ 200/-
Inside Cover	Rs. 3000/-	US \$ 150/-
Full page	Rs. 2000/-	US \$ 100/-
Half page	Rs. 1500/-	US \$ 60/-

Discount of 20% is admissible for 4 successive insertions.

The submission of papers and all other correspondence regarding the Journal may please be addressed to :

Publication Secretary
Journal of Pure and Applied Ultrasonics
C/o Ultrasonics Society of India
CSIR-National Physical Laboratory
Dr. K.S. Krishnan Road, New Delhi-110012
publicationsecretary.usi@gmail.com
www.ultrasonicsindia.org

Journal of Pure and Applied Ultrasonics

VOLUME 39

NUMBER 1

JANUARY-MARCH 2017

CONTENTS

Acoustical and excess parameters in binary liquid mixture at temperature 303.15 K Pallavi B. Nalle, B.R. Shinde, S.U. Shinde, R.G. Dorik and K.M. Jadhav	1
Thermo-acoustical study of strong electrolytes-metal chlorides in aqueous acetone media at different temperatures Bidyadhar Swain, Rabindra N. Mishra and Upendra N. Dash	8
Ultrasonic characterization of extractant for rare earth elements Ranjeeta Giri and Ganeswar Nath	13
Density and speed of sound of binary liquid systems in temperature range 288.15 to 318.15 K Vivek Kumar Pundhir, V.S. Gangwar and Rajeev Kumar Shukla	18
Acoustical parameters of binary mixture of pyridine and carbon tetrachloride Dharamvir Singh Ahlawat and Mahipal Singh Gill	23
Characteristics of an ultrasonic array transmitter in the short range Sahdev Kumar and Hideo Furuhashi	27
PhD Thesis Summary Ultrasonic Nondestructive Evaluation of Type 316 Austenitic Stainless Steel by Time-Frequency Analysis Methods	34

(Authors have stated that the papers have not been published elsewhere)

Acoustical and excess parameters in binary liquid mixture at temperature 303.15 K

Pallavi B. Nalle¹, B.R. Shinde², S.U. Shinde³, R.G. Dorik⁴ and K.M. Jadhav^{5,*}

¹Department of Physics, Shivchhatrapati College, Aurangabad-431003, India

²Department of Physics, Sanjivani Rural Educational Society, College of Engineering, Kopargaon-423603, India.

³Department of Physics, Pratishtan Mahavidyalaya, Paithan, Aurangabad-431107, India.

⁴Department of Physics, Vivekananda College, Aurangabad-431001, India.

^{5*}Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad-431004, India

*E-mail: drjadhavkm@gmail.com

Acoustical and excess parameters have been calculated from the experimentally measured data of ultrasonic velocity, density and viscosity in binary liquid mixtures containing herbal extract of drug *Piper Nigrum* with $ZnCl_2$ over the composition range (number of moles (n) of drug = 0.7009, 1.4018, 2.1027, 2.8036 and 3.5045) at 303.15 K temperature. Obtained results are fitted to the Redlich - Kister polynomial equation. These results have been explained on the basis of the intermolecular interactions present in the liquid mixtures. Present investigation provides important information about the physiological system and used to understand the mechanism of their metabolism in the living system.

Keywords: Ultrasonic velocity, density, adiabatic compressibility, excess intermolecular free length, molecular interaction.

Introduction

Physico-chemical behaviour of liquid mixtures can be characterized by ultrasonic tool¹. The study of molecular interaction between the components of pure, binary and ternary liquid mixtures, using ultrasonic speed and thermodynamic parameters derived from it, has been the aim of several earlier researchers². Excess functions are found to be very sensitive towards mutual interaction between component molecules of the liquid mixture. The sign and the extent of deviation of these functions from ideality depend on the strength of interactions between unlike molecules. The sign and magnitude of excess parameters have been used to investigate the interactions between the components of a system³. The deviation from the law of additivity in the excess values of parameters indicate the presence of interactions between constituents of liquid mixtures. The literature survey reveals that no work is done in binary liquid mixture containing herbal extract of drug *Piper Nigrum* with $ZnCl_2$. Drug *Piper Nigrum* is commonly known as black pepper⁴. Black pepper is the dried fruit of *Piper Nigrum*

Linn. and belongs to flower vine of piperaceae family⁵. *Piper Nigrum* has many medicinal properties such as it is used to treat vertigo, asthma, chronic indigestion, obesity, fever, paralytic, arthritic disorders and also advised in diarrhea and cholera⁶. The main chemical constituents of *Piper Nigrum* L. are the alkaloid piperine (a trans-trans isomer of 1-piperoly piper dine), which has many pharmacological properties. Herbal extract⁷ is a concentrated ingredient of the herb blended with a suitable solvent to preserve the potency of its active ingredients. The significance of herbal extract compared to synthetic drugs is that herbal drugs are absorbed by the body very quickly especially in older adults. Same work, on herbal extract that is a variation of acoustical parameters of herbal extract pomegranate at 4 MHz was carried out by Aswale *et al.*⁸. Zinc Chloride is one of the metal ion (like other metal ions Na^{++} , K^+ , Ca^{++} , Zn^{++} , Cu^{++} , Fe^{++} etc.) in human body⁹. Ethanol is used as a solvent for present investigation. Ethanol is a volatile, colorless liquid that has a slight odor. It is a primary alcohol with 2 carbon structure with the molecular formula CH_3CH_2OH . Alcohols are strongly self

associated liquids having three dimensional network of hydrogen bonding and can be associate with any other group having some degree of polar attraction. Ethanol's hydroxyl group is able to participate in hydrogen bonding¹⁰. Ethanol can dissolve a large number of chemical substances such as alkaloids, alkaloidal salts, tannins. Piperine is pungent alkaloid, insoluble in water and soluble in ethanol¹¹ hence ethanol is used for the extraction of piperine. In the present study the values and variations of excess acoustical parameters like excess ultrasonic velocity (U^E), excess density (ρ^E), excess viscosity (η^E), excess adiabatic compressibility (β^E), excess specific acoustic impedance (Z^E), excess intermolecular free length (L_f^E), excess relaxation time (τ^E), excess relaxation amplitude ($\frac{\alpha^E}{f^2}$) have been reported at 303.15 K.

Materials and Methods

In the present investigation the chemicals used are of AR grade and they are purified by standard procedure¹². The different concentrations of the liquid mixture are prepared by varying number of moles. Stoppard conical flasks are used for preserving the prepared mixtures and the flasks are left undisturbed to attain thermal equilibrium.

Ultrasonic velocity measurement

Ultrasonic interferometer is used for ultrasonic velocities measurements of *Piper Nigrum* extract with metal ion over the composition range (number of moles (n) of drug = 0.7009, 1.4018, 2.1027, 2.8036 and 3.5045) have been measured and all these measurements are done at a fixed frequency of 2 MHz at temperature 303.15 K. The temperature of the pure liquids or liquid mixtures is done by using temperature controlled waterbath by circulating water around the liquid cell which is present in interferometer.

Density measurement

Specific gravity bottle is used for the measurement of densities of pure liquids and liquid mixtures with an accuracy of + or - 0.5%. An electronic weighing balance with a precision of + or - 0.1 mg is used for the measurements of mass of pure liquids or liquid mixtures. Average of 4 - 5 measurements is taken for each sample.

Velocity measurement

Ostwald's viscometer is used for the measurement of viscosity of pure liquids or liquid mixtures. The time of flow of liquid in the viscometer is measured with an electronic stopwatch with a precision of 0.01 s.

Preparation of extract of Piper Nigrum Seeds

Figure 1 shows the structure of *Piperine*. Dried seeds of *Piper Nigrum* of good quality were purchased from the local market. Seeds were ground to coarse powder. 100 gm of powdered seed was boiled with 1 lit of ethanol in a conical flask for 30 min and the liquid was decanted¹³.

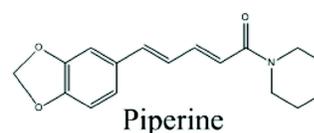


Fig. 1 Structure of *Piperine*

Theoretical Aspects

From the experimental data of ultrasonic velocity (U), density (ρ) and viscosity (η), various acoustic and thermodynamic parameters have been calculated. Acoustical parameters have been calculated by using the following equations¹⁴.

- 1. Adiabatic compressibility (β):** The adiabatic compressibility (β) has been calculated from the ultrasonic velocity (U) and density (ρ) of the medium using the equation as:

$$\beta = \frac{1}{U^2} \quad (1)$$

- 2. Specific Acoustic impedance (Z):** The specific acoustic impedance is given by following equations, where u and ρ are the ultrasonic velocity and density of the liquid respectively.

$$Z = \rho U \quad (2)$$

- 3. Intermolecular free length (L_f):**

$$L_f = K_T \sqrt{\beta} \quad (3)$$

Where K is temperature dependent constant called as Jacobson constant it is 2.075×10^{-6} for 303.15 K

- 4. Relaxation time (τ):** The relaxation time can be calculated from the relation as:

$$\tau = \frac{4}{3} \beta \eta \quad (4)$$

Where, β and η are adiabatic compressibility and viscosity of the liquid mixture.

5. Relaxation amplitude (αf^2): The relaxation amplitude can be calculated from the relation as:

$$\alpha / f^2 = \frac{8\pi^2\eta}{3\rho U^3} \quad (5)$$

Where, η and ρ are viscosity and density of the liquid mixture.

Excess parameters

The corresponding excess thermo-acoustical parameters such as U^E , ρ^E , η^E , β^E , Z^E , L_f^E , τ^E and $\frac{\alpha^E}{f^2}$ have been calculated by using the standard equations. The above excess parameters are fitted to the following Redlich-Kister equation.

$$Y^E = Y_{exp} - (X_1 Y_1 + X_2 Y_2) \quad (6)$$

Where Y^E is U^E or ρ^E or η^E or β^E or Z^E or L_f^E or τ^E or $\frac{\alpha^E}{f^2}$ and X represents number of moles of the component and subscript 1 and 2 stands for component 1 and 2. Y_{exp} is for parameters of mixture or solution.

Results and Discussion

The excess thermo-acoustical parameters which play a major role in understanding the nature of molecular interactions in liquid mixtures have been studied by several workers^{15, 16}. The excess thermo-acoustical parameters are defined as the difference between the experimental values and ideal mixture values. The comparison of experimental values of ultrasonic velocities, densities and viscosities with the literature

values of pure liquid (ethanol) are given in Table 1¹⁷. The experimental values of ultrasonic velocity, density, viscosity and other derived parameters are reported in Table 2.

The variation of ultrasonic velocity as a function of concentration is shown in Fig. 2(a). It can be observed from Fig. 2(a) that ultrasonic velocity increases with *Piper Nigrum* concentration. The increase in ultrasonic velocity is found to be linear this shows that there is moderate attraction between molecules and there is intermolecular interaction exists within the mixture. The linear variation of ultrasonic velocity with concentration indicates the occurrence of complex formation between $ZnCl_2$ and *Piper Nigrum*. Chemical interaction may

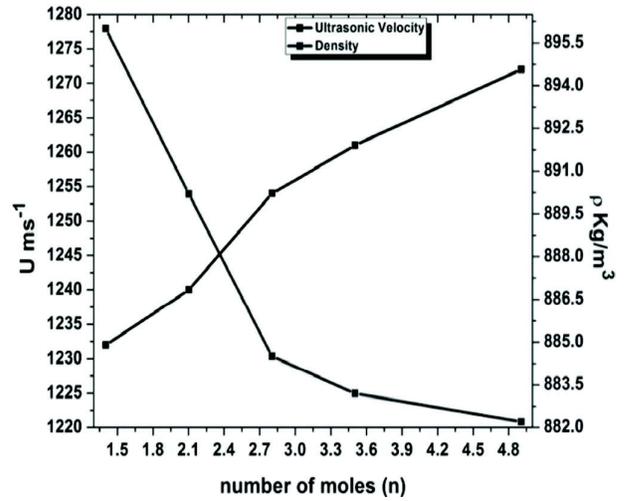


Fig. 2(a) Variations of ultrasonic velocity and density with number of moles (n) of drug *Piper Nigrum*

Table 1 – Values of ultrasonic velocity (U), density (ρ) and viscosity (η) of pure liquid with literature values at temperature T = 303.15 K.

Liquid	(U) m.s ⁻¹		(ρ) kg.m ⁻³		(η) /10 ⁻³ N s.m ⁻²	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
Ethanol	1130	1131.5 [1]	776.2	779.15 [1]	0.9126	0.9122 [1]

Table 2 – The values of thermo-acoustical parameters like ultrasonic velocity (U), density (ρ), viscosity (η), adiabatic compressibility (β), specific acoustic impedance (Z), intermolecular free length (L_f), relaxation time (τ) and relaxation amplitude (αf²) in binary mixture containing (ZnCl₂ + *Piper Nigrum*) at temperature T = 303.15 K.

Number of Moles (n)	(U) m.s ⁻¹	(ρ) Kg.m ⁻³	(η)/10 ⁻⁴ Ns.m ⁻²	(β) × 10 ⁻¹⁰ Kg ⁻¹ ms ²	(Z) × 10 ⁶ kg.m ⁻² s ⁻¹	(L _f) Å	(τ) × 10 ⁻¹³ s	(αf ²)/10 ⁻¹⁵ Npm ⁻¹ s ²
0.7009	1232	896.0	2.7377	7.3531	1.103872	0.56266	2.68421	4.2960
1.4018	1240	890.2	4.5147	7.3058	1.103848	0.56085	4.39801	6.9938
2.1027	1254	884.5	4.7677	7.1896	1.109163	0.55636	4.57060	7.1870
2.8036	1261	883.2	4.9169	7.1205	1.113715	0.55369	4.66833	7.3000
3.5045	1272	882.2	4.7661	7.0058	1.122158	0.54921	4.45226	6.9020

involve due to the association between the ion and dipole molecule. The increase in ultrasonic velocity can be attributed to increase in molecular interaction between *Piper Nigrum* and zinc metal ion. Similar observations of ultrasonic velocity have been reported in the literature¹⁸.

Density of various concentrations of *Piper Nigrum* in $ZnCl_2$ is graphically represented in Fig. 2(a). It is observed that the density decrease with increase in concentration of *Piper Nigrum* in $ZnCl_2$. The decrease in density can be attributed to increase in molecular interaction between *Piper Nigrum* and zinc metal ion and drug acts as structure breaker. Similar observation of density of drug colimax in aqueous mixture of methanol has been reported in the literature¹⁹.

From Fig. 2(b) it is seen that value of viscosity increases with increase in concentration of *Piper Nigrum* drug upto 2.8036 concentration and again viscosity values decreases for 3.5045 concentration. It suggests that the existed intermolecular interaction becomes weak with increasing concentration and existed interaction becomes strong at last concentration²⁰.

The adiabatic compressibility decreases with decreases in concentrations of *Piper Nigrum* is shown in Fig. 2(b). It indicates that there is strong solute solvent interaction. The solution becomes more and more compressible as adding the concentration of drug *Piper Nigrum*²¹.

Specific acoustic impedance (Z) is governed by inertial and elastic properties of the medium.

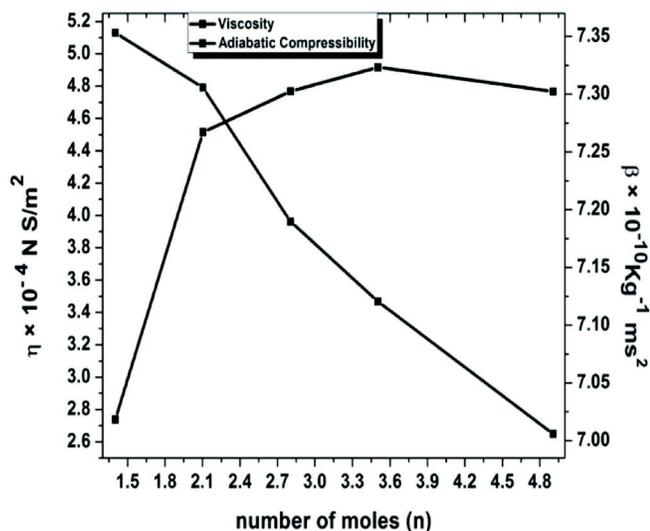


Fig. 2(b) Variations of viscosity and adiabatic compressibility with number of moles (n) of drug *Piper Nigrum*

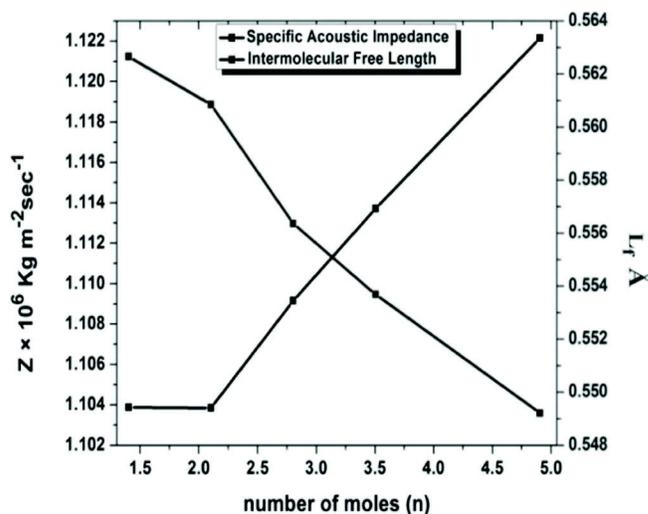


Fig. 2(c) Variations of specific acoustic impedance and intermolecular free length with number of moles (n) of drug *Piper Nigrum*

Table 2 and Fig. 2(c) show that the value of specific acoustic impedance increases with increase in concentration. The increase in specific acoustic impedance may be due to increase in molecular interaction between *Piper Nigrum* and zinc metal ion. It shows that there is increase in interactions within *Piper Nigrum* and Zn^+ metal ions²².

The values of intermolecular free length (L_f) shown in Table 2 and graphically represented in Fig. 2 (b). It is observed that values of intermolecular free length decrease with increasing concentration of *Piper Nigrum* due to comple formation. The observed behaviour shows that there is enhanced molecular association which is similar for antibiotic drug ampicillin sodium system²³.

From Fig. 2(d) it is observed that the relaxation time increases with increase in concentration of drug *Piper Nigrum* upto 2.8036 concentration and again relaxation time values decreases for 3.5045 concentration²⁴. This indicates the presence of molecular interaction between Zn^{++} ions and *Piper Nigrum*. Fig. 2(d) also represents similar behaviour of relaxation amplitude. The increase in relaxation amplitude can be attributed to increase in molecular interaction between *Piper Nigrum* and zinc metal ion²⁵.

The variation of excess values (U^E , ρ^E , η^E , β^E , Z^E , L_f^E , τ^E and $\frac{\alpha^E}{f^2}$) with the number of moles of drug *Piper Nigrum* ranging from 0.7009 to 3.5045 (at equal interval of 0.7009) at 303.15 K temperature are as shown in Table 3.

Table 3 – The values of excess thermo-acoustical parameters like excess ultrasonic velocity (U^E), excess density (ρ^E), excess viscosity (η^E), excess adiabatic compressibility (β^E), excess specific acoustic impedance (Z^E), excess intermolecular free length (L_f^E), excess relaxation time (τ^E), excess relaxation amplitude $\frac{\alpha^E}{f^2}$ of $ZnCl_2 + Piper Nigrum$ herbal extract at temperature $T = 303.15$ K.

Number of Moles (n)	(U^E) m.s ⁻¹	(ρ^E) kg.m ⁻³	$(\eta^E)\times 10^{-4}$ Ns.m ⁻²	$(\beta^E)\times 10^{-10}$ kg ⁻¹ ms ²	$(Z^E)\times 10^6$ Kg.m ⁻² s ⁻¹	(L_f^E) Å	$(\tau^E)\times 10^{-13}$ s	$\frac{\alpha^E}{f^2}/10^{-15}$ Npm ⁻¹ s ²
0.7009	92.52	0.1181142	-2.812152	0.636121703	-8.869	1.12612945	-0.738092	-1.2786307
1.4018	98.53	0.1131942	-1.008588	0.631896293	-8.879	1.12218368	-0.727421	-1.2570956
2.1027	110.1	0.1071616	-0.725019	0.620541522	-8.896	1.10867218	-0.721073	-1.2440607
2.8036	115.9	0.1083918	-0.55238	0.611907113	-8.903	1.09846614	-0.716488	-1.2347425
3.5045	126	0.1050729	-0.686044	0.602516664	-8.909	1.08714848	-0.713129	-1.2279111

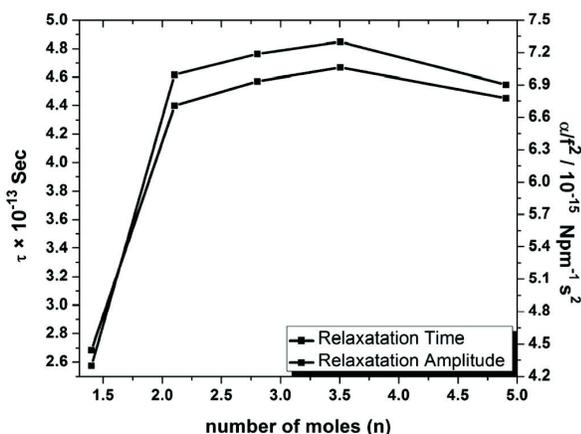


Fig. 2(d) Variations of relaxation time and relaxation amplitude with number of moles (n) of drug *Piper Nigrum*

From Fig. 3(a), it is clear that the values of excess ultrasonic velocity (U^E) and excess density (ρ^E) are positive and increases at all increasing concentration of drug. This indicates that the molecular interaction between drug *Piper Nigrum* and Zn^{++} metal ion is more stronger²⁶.

Fig. 3(b) represents the variation of excess viscosity (η^E) with the number of moles of drug *Piper Nigrum*. Negative variations are observed in Fig. 3(b). The negative variations, confirm that there exist dispersion and dipolar forces in the components of liquid mixtures²⁷.

The variations in excess adiabatic compressibility (β^E) with number of moles are presented in Fig. 3(b). It is observed that the values of β^E are positive at all concentration. The positive values of β^E for the system suggest the presence of weak interaction between unlike molecules. The size of component molecules almost not equal, it is seen that their molecules do not pack well into each other's structures. This results in expansion of volume and hence positive β^E ²⁸.

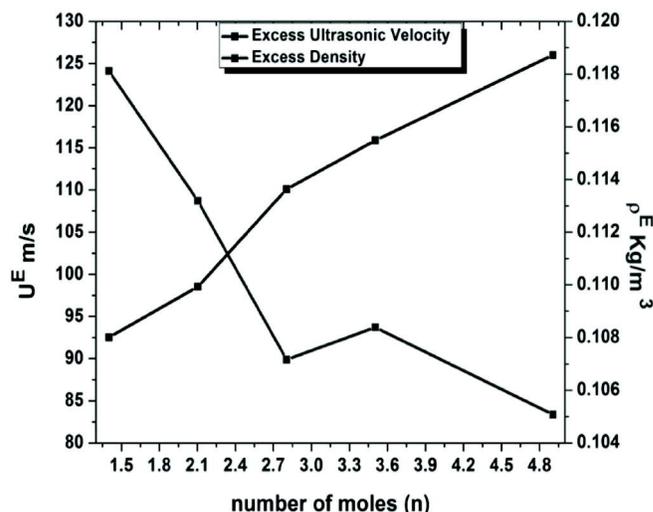


Fig. 3(a) Variations of excess ultrasonic velocity and excess density with number of moles (n) of drug *Piper Nigrum*

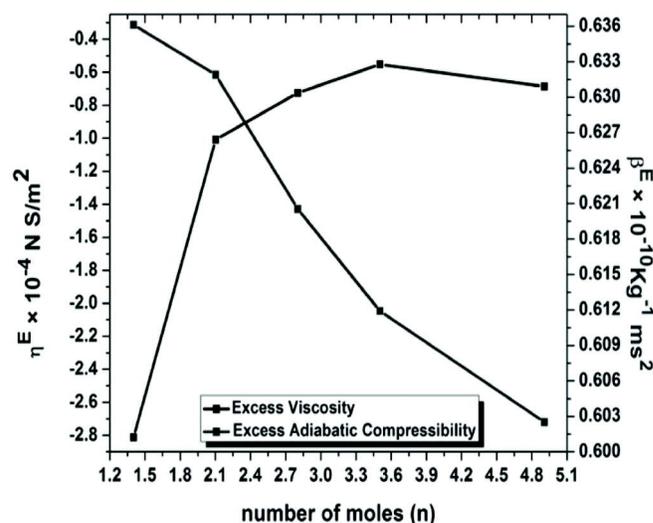


Fig. 3(b) Variations of excess viscosity and excess adiabatic compressibility with number of moles (n) of drug *Piper Nigrum*

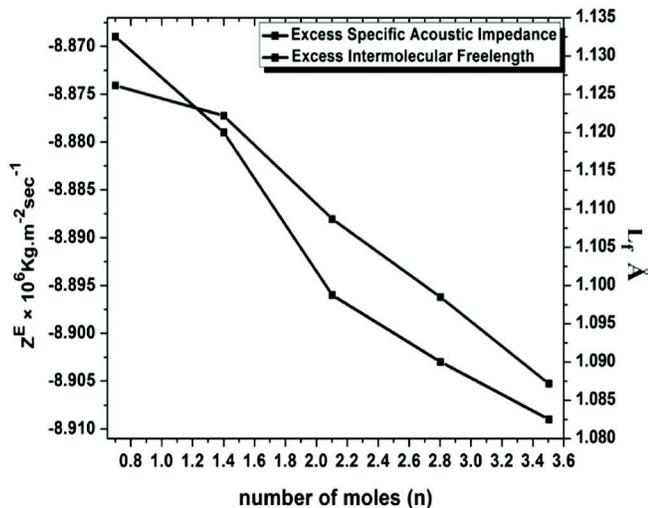


Fig. 3(c) Variations of excess acoustic impedance and excess intermolecular free length with number of moles (n) of drug *Piper Nigrum*

The variations in excess specific acoustic impedance (Z^E) with number of moles are presented in Fig. 3 (c). It is observed that the values of Z^E are negative at all concentration. The negative values of Z^E for the system suggest the presence of weak interaction between unlike molecules²⁹.

The changes in excess intermolecular free length (L_f^E) have been calculated with the help of Eq. (4). The values of L_f^E are shown in Table 3. As the number of moles increases L_f^E becomes positive showing weak interaction between solute and solvent particles, as well as small interstitial accommodation of drug *Piper Nigrum* molecules in zinc chloride solution. This trend suggests that hetero association and homo association of

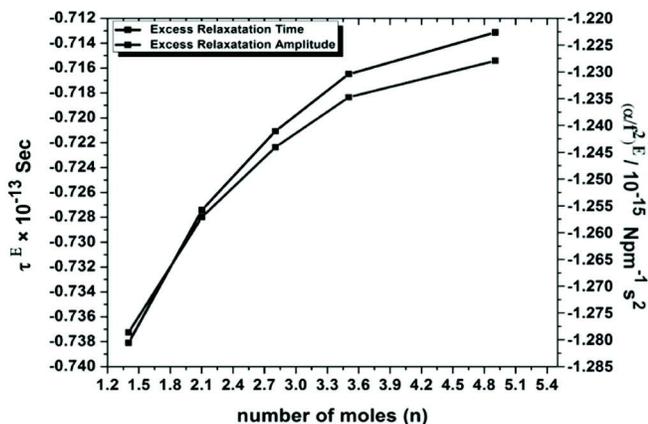


Fig. 3(d) Variations of excess relaxation time and excess relaxation amplitude with number of moles (n) of drug *Piper Nigrum*

molecular decreases. However the excess in free length shows positive values but the changes are very small³⁰.

The variations in excess relaxation amplitude (α^E) and excess relaxation time (τ^E) are presented in Fig. 3 (d). It is observed that the values are negative at all concentration.

Conclusion

The extraction of *Piper Nigrum* is successfully prepared and same is used to reconstitutes in aqueous 1 molar solution of ZnCl_2 with different concentration. Ultrasonic velocity increases with *Piper Nigrum* drug concentration. It is observed that there exist specific strong molecular interactions between the components of the liquid mixture studied. Due to presence of drug *Piper Nigrum*, zinc chloride structure breaks and there is a formation of complex between constituents. *Piper Nigrum* acts as structure breaker. The present study of molecular interaction of zinc ions and antioxidant *Piper Nigrum* using ultrasonic investigations provides important information about the physiological system and used to understand the mechanism of their metabolism in the living system.

References

- 1 **Chiappe C. and Rajamani S.**, Structural effects on the physico chemical and catalytic properties of acidic ionic liquids: An Overview, *Eur. J. Org. Chem.* **2011** (2011) 5517-5539.
- 2 **Hawrylak B., Gracie K. and Palepu R.**, Ultrasonic velocity and volumetric properties of isomeric butanediols plus water systems, *Can. J. Chem.* **76** (1998) 464-468.
- 3 **Mehra R. and Sajjani H.**, Acoustical parameters of CuCl-KCl system in acetonitrile-water solvent mixture, *Phys. Chem. Liq.* **39** (2001) 581-588.
- 4 **Panda S. and Kar A.**, Water and ethanol extracts of Piper nigrum in regulating thyroid function and lipid peroxidation in mice, *Pharma. Bio.* **41** (2003) 479-482.
- 5 **Al-Moflehi A., Alhaider A. and Mossa J., Al-Sohaibani M., Rafatullah S. and Qureshi S.**, Inhibition of gastric mucosal damage by Piper nigrum (Black pepper) pretreatment in Wistar albino rats, *Pharma. Mag.* **1** (2005) 64.
- 6 **Yang J.-z., Chang X.-h. and Lu X.-m.**, Thermodynamics of ion pair of magnesium sulfate in mixed solvent, *Chem.*

- Res. in Chinese Univers.* **22** (2006) 403-405.
- 7 **Ong E.S.**, Extraction methods and chemical standardization of botanicals and herbal preparations, *J. Chrom. B* **812** (2004) 23-33.
 - 8 **Aswale S., Aswale S.S., Gowardipe V. and Yavatmal W.D.**, Variation of acoustical parameters of herbal extract pomegranate solutions at frequency 4 MHz, *Int. J. Chem. Physic. Sci.* **4** (2015) 308-313.
 - 9 **Kavanagh J.**, Sodium, potassium, calcium, magnesium, zinc, citrate and chloride content of human prostatic and seminal fluid, *J. Reprod. Fert.* **75** (1985) 35-41.
 - 10 **Mazik M., Cavga H. and Jones P.G.**, Molecular recognition of carbohydrates with artificial receptors: mimicking the binding motifs found in the crystal structures of protein-carbohydrate complexes, *J. Am. Chem. Soc.* **127** (2005) 9045-9052.
 - 11 **Bhaskar V. and Patel P.**, Formulation and evaluation of reservoir type transdermal patches of 18-B-glycyrrhetic acid with piperine as bioenhancer, *Ind. Am. J. Pharm. Res.* **4** (2014) 1298-1308.
 - 12 **Das B., Muhuri P. and Hazra D.**, Ultrasonic studies on alkali metal bromides in 2-methoxyethanol at 25°C, *Acoust. Lett.* **18** (1994) 69-73.
 - 13 **Shamkuwar P.B., Shahi S.R. and Jadhav S.T.**, Evaluation of anti diarrhoeal effect of black pepper (*Piper nigrum* L.), *Asian J. Plant Sci. Res.* **2** (2012) 48-53.
 - 14 **Suryanarayana C. and Kuppusamy J.**, Free volume and internal pressure of liquid from ultrasonic velocity, *J. Acoust. Soc. Ind* **4** (1976) 75.
 - 15 **Polák J., Murakami S., Lam V., flug H. P. and Benson G.**, Molar excess enthalpies, volumes, and Gibbs free energies of methanol-isomeric butanol systems at 25°C, *Can. J. Chem.* **48** (1970) 2457-2465.
 - 16 **Prakash O. and Darbari S.**, Excess thermodynamic properties of binary liquid mixtures, *Acoust. Lett.* **12** (1988) 35-39.
 - 17 **Naidu P.S. and Prasad K.R.**, Ultrasonic velocity and allied parameters in solutions of cypermethrin with xylene and ethanol, *Indian J. Pure Appl. Phys.* **42** (2004) 512-517.
 - 18 **Rassing J. and Attwood D.**, Ultrasonic velocity and light-scattering studies on the polyoxyethylene-polyoxypropylene copolymer Pluronic F127 in aqueous solution, *Int. J. Pharm.* **13** (1982) 47-55.
 - 19 **Wadi R.K. and Ramasami P.**, Partial molal volumes and adiabatic compressibilities of transfer of glycine and DL-alanine from water to aqueous sodium sulfate at 288.15, 298.15 and 308.15 K, *J. Chem. Soc., Faraday Transac.* **93** (1997) 243-247.
 - 20 **Hammes G.G. and Schimmel P.R.**, An investigation of water-urea and water-urea-polyethylene glycol interactions, *J. Am. Chem. Soc.* **89** (1967) 442-446.
 - 21 **Rao N. and Verrall R.E.**, Ultrasonic velocity, excess adiabatic compressibility, apparent molar volume, and apparent molar compressibility properties of binary liquid mixtures containing 2-butoxyethanol, *Can. J. Chem.* **65** (1987) 810-816.
 - 22 **Nithya R., Nithyanantham S., Mullainathan S. and Rajasekaran M.**, Ultrasonic investigation of molecular interactions in binary mixtures at 303 K, *J. Chem.* **6** (2009) 138-140.
 - 23 **Awasthi A. and Shukla J.**, Ultrasonic and IR study of intermolecular association through hydrogen bonding in ternary liquid mixtures, *Ultrasonics* **41** (2003) 477-486.
 - 24 **Kessler L. and Dunn F.**, Ultrasonic investigation of the conformational changes of bovine serum albumin in aqueous solution, *J. Phys. Chem.* **73** (1969) 4256-4263.
 - 25 **Nithyanantham S. and Palaniappan L.**, Thermodynamical and excess thermoacoustical study on some monosaccharide (glucose) with enzyme amylase in aqueous media at 298.15 K, *Eur. Phys. J. Appl. Phys.* **53** (2011) 31101.
 - 26 **Rastogi M., Awasthi A., Gupta M. and Shukla J.**, Ultrasonic investigations of X... HO bond complexes, *Indian J. Pure Appl. Phys.* **40** (2002) 256-263.
 - 27 **Fort R. and Moore W.**, Viscosities of binary liquid mixtures, *Transact. Faraday Soc.* **62** (1966) 1112-1119.
 - 28 **G. Arul. and L. Palaniappan.**, Molecular interaction studies in the ternary mixture of cyclohexane+ toluene+ 2-propanol, *Indian J. Pure Appl. Phys.* **39** (2001) 561-564.
 - 29 **Thirumaran S. and George D.**, Ultrasonic study of intermolecular association through hydrogen bonding in ternary liquid mixtures, *ARPNI J. Eng. Appl. Sci.* **4** (2009) 1-11.
 - 30 **Sumathi T. and Maheswari J.U.**, Ultrasonic and theoretical studies of some ternary liquid mixtures at various temperatures, *Indian J. Pure Appl. Phys.* **47** (2009) 782-786.

Thermo-acoustical study of strong electrolytes-metal chlorides in aqueous acetone media at different temperatures

Bidyadhar Swain^{1,*}, Rabindra N. Mishra² and Upendra N. Dash³

¹Department of Physics, DRIEMS, Cuttack-754022, India

²PG Department of Physics, Ravenshaw University, Cuttack-753003, India

³Plot No.436, Chakeisihani, Bhubaneswar-751010, India

*E-mail: bidya.swain11@gmail.com

The ultrasonic velocity, density and viscosity measurements have been made on strong electrolytes like strontium chloride, cadmium chloride and barium chloride in 5, 10 and 15 wt% of aqueous acetone solvent systems in different concentrations over the temperature range 298.15K to 313.15K at 5K interval. From the experimental data, various thermo-acoustical parameters, such as acoustic impedance, isentropic compressibility, intermolecular free length, relaxation time, Gibb's free energy change, ultrasonic attenuation, internal pressure, and free volume have been computed to investigate the ion-solvent and solvent-solvent interactions in these systems. It is observed that the ion-solvent and solvent-solvent interactions depend on concentration, temperature, ionic size and nature of the electrolyte. The structural arrangement of molecules in electrolyte solutions has been discussed on the basis of electrostatic field. The qualitative intermolecular elastic forces between the solute and solvent molecules are explained in terms of compressibility.

Keywords: Acoustic impedance, internal pressure, relaxation time, ultrasonic attenuation, Gibb's free energy.

Introduction

Ultrasonic studies are widely employed to assess the acoustic properties and predict the intermolecular interactions in the liquid mixture and ionic interactions in electrolytic solutions¹⁻². Ultrasonic velocity together with density, viscosity and related acoustic parameters of electrolytes in mixed solvent systems assist in characterizing the structure and physical properties of solutions. The investigation of ultrasonic velocity and thermo-acoustic properties of electrolytes in aqueous and mixed solvent system has been the area of interest of many researchers³.

In continuation of our earlier work in aqueous medium⁴, the present investigation deals with the study of molecular interactions of strong electrolytes (strontium chloride, cadmium chloride and barium chloride) in 5, 10 and 15 wt% aqueous acetone solvent systems in different concentrations over the temperature range 298.15K to 313.15K at 5K interval. Various thermo-acoustical parameters, such as acoustic impedance (Z),

isentropic compressibility (K_s), intermolecular free length (L_f), relaxation time (τ), Gibb's free energy change (ΔG), ultrasonic attenuation (α/f^2), internal pressure (π_i) and free volume (V_f) have been computed from ultrasonic velocity (U), density (d) and viscosity (η) data which provide qualitative information regarding molecular interactions. The chemicals used in the work have wide applications in pharmaceutical, medicinal, agricultural, environmental, industry, etc.

Materials and Methods

All electrolytes like strontium chloride, cadmium chloride and barium chloride used were of GR or AR grades obtained from Merck and dried over anhydrous CaCl_2 in desiccator before use. Acetone from Merck with purity $\geq 99\%$ was directly used without further purification. Conductivity water (Sp. cond. $\sim 10^{-6}$ S.cm⁻¹) was used for preparing water + acetone (5, 10 and 15 wt%) mixtures. The acetone content in the mixed solvents was accurate within $\pm 0.01\%$ and solutions were used on the same day. The solutions were prepared on the molal

basis and conversion of molality to molarity was done by using standard expression and the density data at the corresponding temperature. The solute content of the solutions varied over a concentration range of 6.0×10^{-3} M to 8.0×10^{-2} M for all measurements.

Velocity measurement

Ultrasonic velocity measurements in the solutions were made by using a multi frequency ultrasonic interferometer operating at a frequency of 2MHz at different temperatures ranging from 298.15K to 313.15K at 5K intervals. The temperature was controlled by a thermostat accurate to within ± 0.05 K. The precision of the ultrasonic velocity measurements was within ± 0.5 ms^{-1} .

Density measurement

The densities of solutions were measured by relative measurement method using a specific gravity bottle (25ml capacity). At least five observations were taken and the differences in any two readings did not exceed $\pm 0.02\%$.

Viscosity measurement

Viscosity measurements were made as described earlier⁹ using an Ostwald viscometer in a water thermostat whose temperature was controlled to ± 0.05 K and efflux time was determined using a digital stop clock with an accuracy of ± 0.01 s. An average of three sets of flow times for each solution was taken for the calculation of viscosity. The values of viscosity so obtained were accurate to within $\pm 0.3 \times 10^{-3}$ Cp.

Theoretical aspects

From the ultrasonic velocity (U), density (d) and viscosity (η) data following parameters have been calculated⁵⁻⁶.

$$\text{Acoustic impedance : } Z = Ud \quad (1)$$

$$\text{Isentropic compressibility : } K_s = 1/U^2d \quad (2)$$

$$\text{Intermolecular free length : } L_f = K_T \sqrt{K_s} \quad (3)$$

$$\text{Relaxation time : } \tau = 4\eta/3U^2d \quad (4)$$

$$\begin{aligned} \text{Gibb's free energy change :} \\ \Delta G = k_B T \ln(k_B T \tau / h) \end{aligned} \quad (5)$$

$$\text{Ultrasonic attenuation : } \alpha/f^2 = 4\pi^2 \tau / 2U \quad (6)$$

Internal pressure :

$$\pi_i = b RT (K\eta/U)^{1/2} (d^{2/3}/M_{eff}^{7/6}) \quad (7)$$

$$\text{Free volume : } V_f = (M_{eff} U / K\eta)^{3/2} \quad (8)$$

where $M_{eff} = \sum ni mi / \sum ni$ is the effective molecular weight, $K_T = (93.875 + 0.375T) \times 10^{-8}$ is the temperature dependent Jacobson's constant, $b'=2$ is the cubic packing factor for all liquids, T is the temperature in Kelvin, α is the attenuation co-efficient and f' is the frequency of ultrasonic wave ($=2\text{MHz}$), $k_B = 1.38 \times 10^{-23}$ JK^{-1} molecule⁻¹ is the Boltzmann's constant, $h = 6.626 \times 10^{-34}$ Js is the Planck's constant, $R = 8.3143 \text{JK}^{-1} \text{mol}^{-1}$ is the universal gas constant, $K = 4.281 \times 10^9$ is the dimensionless constant independent of temperature and nature of liquid.

Results and Discussion

As observed previously⁴, the values of ultrasonic velocity (U) increase with the increase of acetone content in water as well as the concentrations of electrolytes (Metal chlorides) in various solvent systems (5, 10, and 15 wt% of acetone + water). Ultrasonic velocity tends to increase due to increase in molecular mass of electrolytes and it also increases with increase in temperature in all the solvent systems. With increase in temperature, the reoccurs a structural arrangement leading to a comparatively more order state resulting in increase in velocity. It also suggests that disruption of water structure is enhanced with the addition of acetone and electrolyte. This is well agreeing with the earlier studies in various mixed solvent systems⁶⁻⁷. The density (d) and viscosity (η) of the electrolytes (strontium chloride, cadmium chloride and barium chloride) in aqueous acetone increase with the increase in

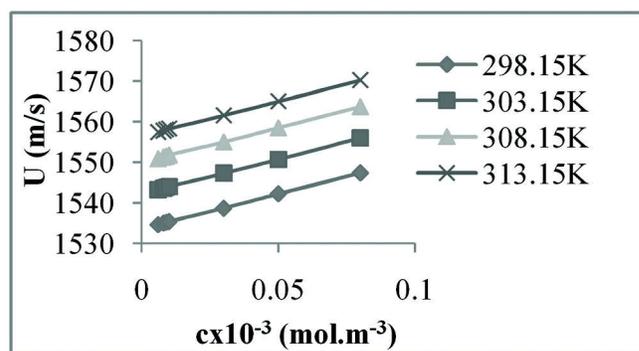


Fig. 1(a) Plot of U versus c for SrCl_2 in 5 wt% acetone + water at different temperatures.

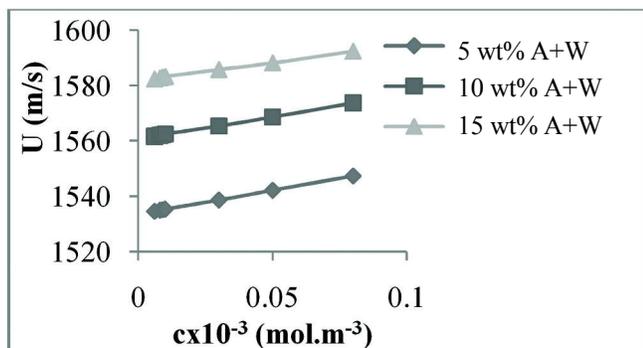


Fig. 1(b) Plot of U versus c for SrCl_2 in different aqueous acetone solution at 298.15K.

concentration of solution due to association occurs between solute and solvent molecules⁸ and decrease with rise of temperature due to thermal energy of the system which diminishes the intermolecular forces⁹. Typical plots of ultrasonic velocity (U) versus concentration (c) are shown in Fig. 1(a)-(b).

From Fig. 2(a)-(b), it is observed that the acoustic impedance (Z), which determines the elastic property (*i.e.*, the bulk modulus of elasticity) of the medium increases with increase in acetone content in water and concentration of electrolytes in all the solvent systems⁵. This is well agreeing with the theoretical requirement as density and ultrasonic velocity increase with increase in the concentration of electrolytes. The increase in Z values with concentration of electrolytes at all temperatures may be attributed to the effective solute-solvent interactions. The Z values also increase with increase in temperature due to structural properties of electrolyte in the solution and there occurs a structural rearrangement as a result of solvation leading to a comparatively more ordered state¹⁰. Since Z is a function of elastic property of the medium and depends on the structural changes of the

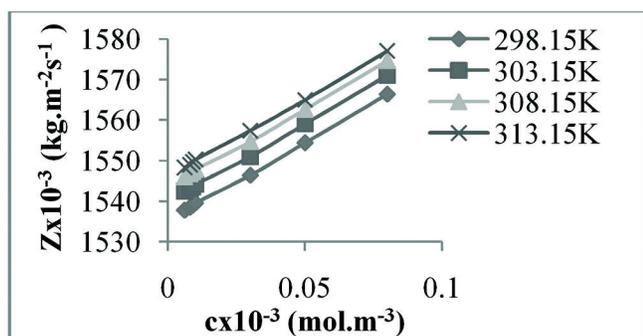


Fig. 2(a) Plot of Z versus c for CdCl_2 in 10 wt% acetone + water at different temperatures.

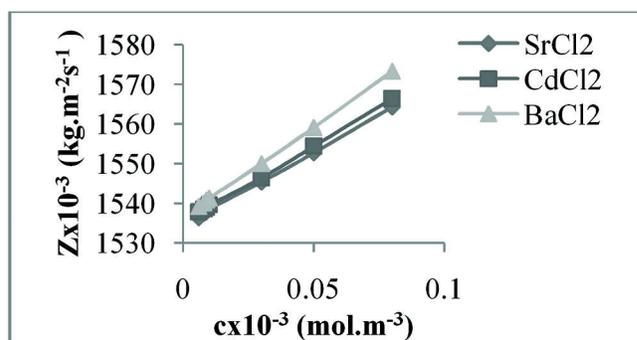


Fig. 2(b) Plot of Z versus c for different electrolytes in 10 wt% acetone + water at 298.15K.

solution, the higher Z values in aqueous acetone solution as compared to that in water⁴ and increasingly higher values with increase in the concentration of electrolytes and also with increase in acetone content in water suggest the solution medium in each case starts gaining its elastic behaviour. Z increases with increase in temperature, as ultrasonic velocity increases with temperature. The Z values of electrolytes in all solvent systems are in the order: $\text{SrCl}_2 < \text{CdCl}_2 < \text{BaCl}_2$. Typical plots of Z versus c are shown in Fig. 2(a)-(b).

It is observed that, the isentropic compressibility (K_s) decreases as the concentration of electrolytes increases and also with increase in acetone content in water at all temperatures. The decrease in K_s with concentration is due to the interstitial spaces in water are occupied by the solute molecules making the medium less compressible, *i.e.*, providing greater electrostriction. This is possible due to electrostatic field of ion causing compactness of the medium due to ion-solvent interaction. Further, the decrease in K_s with increase in acetone content in water due to filling of the interstitial spaces in water by organic co-solvent molecules thereby making a tight structure. Hence K_s describes the molecular arrangement in the solution medium. The value of K_s also decreases with increase in temperature in all the solvent systems. Because the compression of the medium becomes more prominent resulting decrease in K_s values⁶.

From Fig. 3(a)-(b), it is observed that the intermolecular free length (L_f) decreases with increase in concentration and increase in acetone content in water at all temperatures. The decrease of L_f with increase of concentration indicates that there is a significant interaction between solute and solvent suggesting the structure promoting behaviour on addition of

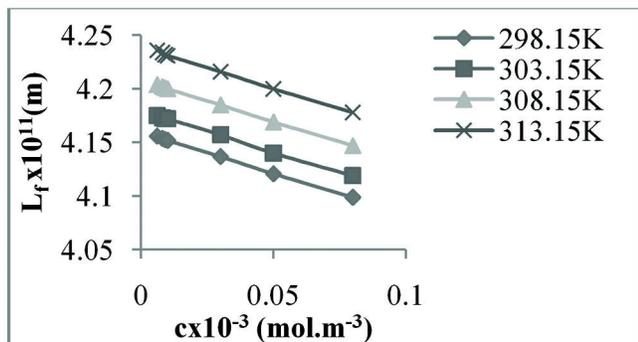


Fig. 3(a) Plot of L_f versus c for BaCl_2 in 15 wt% acetone + water at different temperatures.

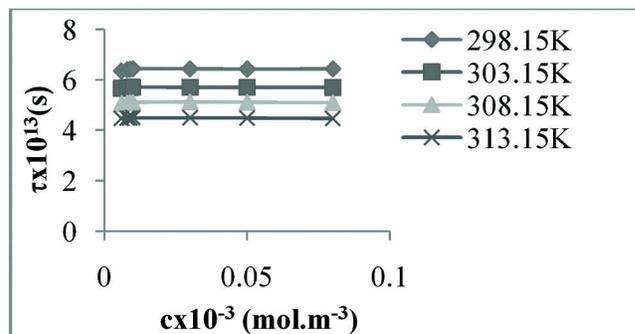


Fig. 4(a) Plot of τ versus c for SrCl_2 in 10 wt% acetone + water at different temperatures.

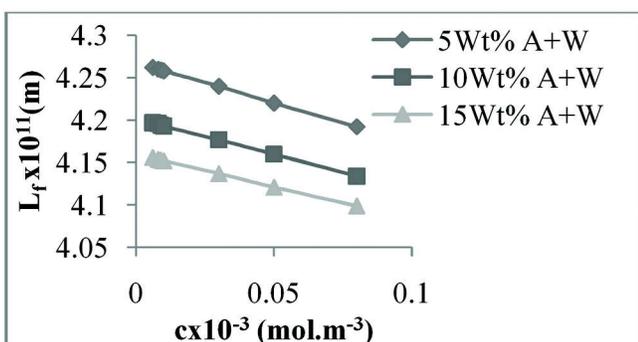


Fig. 3(b) Plot of L_f versus c for BaCl_2 in different aqueous acetone solution at 298.15K.

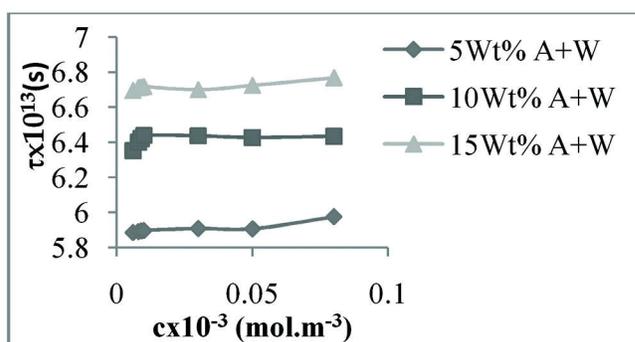


Fig. 4(b) Plot of τ versus c for SrCl_2 in different aqueous acetone solution at 298.15K.

electrolytes¹¹. Further, the decrease of L_f with increase of acetone content in water may be due to the effective solvent-solvent interaction in the solution and decrease in isentropic compressibility, *i.e.*, $L_f = K_T \sqrt{K_s}$

The increase of temperature increases the thermal energy of the system and decreases the intermolecular forces thereby causing an expansion in volume and decrease in density, and hence, free length increases. Therefore, intermolecular free length increases with increase in temperature. The intermolecular free length of one electrolyte in aqueous acetone solution is less than the other is due to the less isentropic compressibility value of former than the latter. Typical plots of L_f versus c are shown in Fig. 3(a)-(b).

The relaxation time (τ) increases with increase in concentration of electrolytes in all aqueous acetone media at all temperatures (except in few cases) suggesting the rearrangement of molecules due to co-operation process and reinforcement of H-bonds^{12, 13}. With rise in temperature, H-bonds become weak due to thermal vibration resulting in structure breaking effect that

predominates over H-bond formation, and hence, τ decreases with temperature in the entire electrolyte in all aqueous acetone media¹⁴. Also τ increases with increase in acetone content in water for all electrolytes at all temperatures. Typical plots of τ versus c are shown in Fig. 4(a)-(b).

Gibb's free energy change (ΔG) increases with increase in concentration of electrolytes (except in few cases) at all temperatures in all solvent systems. This suggests shorter time for rearrangement of molecules. With rise in temperature, ΔG decreases due to increase in kinetic energy of the molecules by thermal energy and takes longer time for rearrangement of molecules for a given concentration in all the solvent systems¹⁵. Also ΔG increases with increase in acetone content in water. Ultrasonic attenuation increases with increase in acetone content in water and concentration of electrolytes (except in few cases), but it decreases with rise in temperature for all the electrolytes in all the solvent systems.

As observed, the free volume (V_f) decreases with increase in concentration and increases with temperature

for all solvent system. Further, it increases with increase in acetone content in water. Internal pressure (π_i) changes in a manner opposite to that of free volume at all temperatures. The decrease of V_f (or increase of π_i) indicates the formation of hard and/or tight solvation layer around the ion¹⁶. With increase in temperature, thermal energy of the molecules increases, hence available free volume (V_f) increases (or decreases).

Conclusion

The results of the present investigation reveal that solute-solvent and solvent-solvent interactions play a vital role for explaining the different thermo-acoustical parameters of strong electrolytes in different aqueous acetone media at four different temperatures 298.15K, 303.15K, 308.15K and 313.15K. These interactions result in attractive forces which promote the structure forming tendency. It is also noticed that the strength of molecular interaction weakens with rise of temperature which may be due to weak intermolecular forces and thermal energy of the system. The decrease in the value of isentropic compressibility with increase in concentration is due to the occupation of the interstitial spaces of water by the solute molecules thereby making the medium less compressible.

Acknowledgements

The authors thankfully acknowledge the support and facilities provided by DRIEMS, Tangi, Cuttack, India to carry out the research work in the institution.

References

- 1 **Nithiyantham S.** and **Palaniappan L.**, Acoustical studies on some disaccharides (sucrose, lactose, maltose) in aqueous media at room temperature, *Metals Mat. Proces.*, **20** (2008) 203-208.
- 2 **Dash U.N., Roy G.S.** and **Mohanty S.**, Ultrasonic studies on sodium thiosulphate and ammonium thiosulphate in water and water + acetone mixtures, *Indian J. Chem. Technol.*, **11** (2004) 178-184.
- 3 **Ravichandran S.** and **Ramanathan K.**, Ultrasonic investigations of $MnSO_4$, $NiSO_4$ and $CuSO_4$ aqueous in polyvinyl alcohol solution at 303K, *Rasayan J. Chem.*, **3** (2010) 375-384.
- 4 **Swain B., Mishra R.N.** and **Dash U.N.**, Ultrasonic studies on molecular interactions in strong electrolytes-Metal chlorides in aqueous medium at different temperatures and 2MHz frequency, *Int. J. Adv. Res.*, **4** (2016) 427-439.
- 5 **Moharatha D., Talukdar M., Roy G.S.** and **Dash U.N.**, Evaluation of acoustic parameters of halides of alkali metals and ammonium in aqueous and aqueous dextran solutions at 298.15K, *Researcher*, **3** (2011) 6-12.
- 6 **Das S.** and **Dash U.N.**, Evaluation of thermo-acoustic and non-linearity parameter (B/A) of glycine, α -alanine, β -alanine and phenyl Alanine in D-fructose solutions at 298.15K, *Int. J. Pharm. Sci. Rev. Res.*, **21** (2013) 212-220.
- 7 **Dash U.N.** and **Sahu R.**, Ultrasonic studies on ammonium salts in aqueous ethereal solvent systems, *Acoust. Lett.*, **17** (1994) 157-164.
- 8 **Malasane P.R.**, Study of Interactions of tryptophan through acoustic and thermodynamic properties, *Res. J. Chem. Sci.*, **3** (2013) 73-77.
- 9 **Roy M.N., Bhattacharjee A.** and **Chanda R.**, Molecular interactions of selected amino acids in aqueous resorcinol solutions: volumetric, viscometric and acoustic studies, *Indian J. Sci. Technol.*, **2** (2009) 63-72.
- 10 **Palani R.** and **Jayachitra K.**, Ultrasonic studies in ternary electrolytic mixtures at 303, 308 and 313K, *Indian J. Pure Appl. Phys.*, **46** (2008) 251-254.
- 11 **Kanhekar S.R., Pravina P.** and **Govind K.B.**, Thermodynamic properties of electrolytes in aqueous solution of glycine at different temperatures, *Indian J. Pure Appl. Phys.*, **48** (2010) 95-99.
- 12 **Mehra R.** and **Vats S.**, Viscometric, volumetric and thermoacoustic behaviour of amino acids in urea (aq), *Int. J. Adv. Res.*, **2** (2014) 141-157.
- 13 **Ali A., Hyder S.** and **Nain A.K.**, Intermolecular interactions in ternary liquid mixtures by ultrasonic velocity measurements, *Indian J. Phys. B*, **74** (2000) 63-67.
- 14 **Wadekar M.P.**, Thermo acoustical molecular interaction study of azomethine and its Fe(III) metal complex using ultrasonic technique, *J. Chem. Pharm. Res.*, **5** (2013) 37-41.
- 15 **Fort R.J.** and **Moore W.R.**, Adiabatic compressibilities of binary liquid mixtures, *Trans. Faraday Soc.*, **61** (1965) 2102-2111.
- 16 **Syal V.K., Chauhan S.** and **Gautam R.**, Ultrasonic velocity measurements of carbohydrates in binary mixtures of DMSO + H_2O at 25°C, *Ultrasonics*, **36** (1998) 619-623.

Ultrasonic characterization of extractant for rare earth elements

Ranjeeta Giri and Ganeswar Nath*

Department of Physics, Veer Surendra Sai University of Technology
Sambalpur-768018, Odisha, India

*E-mail: ganesh_nath99@yahoo.co.in

The most important application of rare earth element materials (REE) is in use as source of nuclear energy. Reprocessing consists of dissolution of spent nuclear fuel in acid medium and subsequent recovery of fissile materials and other materials by solvent extraction technique. The appearance of 'third phase' and its formation is one of the major problems encountered during extraction of rare earth elements materials. The treatment of suitable extractants and diluents with knowledge of their intermolecular interaction in the third phase is an important step in the extraction process. The extractant like methyl iso butyl ketone (MIBK) with diluents like toluene and kerosene has been undertaken for the study of third phase. The ultrasonic study has been done with binary mixture at temperature 303 K for different frequencies. The ultrasonic velocities, density, viscosity are measured experimentally. The different physico-acoustical parameters computed and explained in terms of molecular interaction. The variation of each parameter provides the optimum suitable blends of the mixture for extraction of REE materials. The efficiency of the extraction is calculated using Nernst distribution law. The result shows good extraction efficiency for blends of MIBK and toluene as compared to kerosene.

Keywords: Rare earth elements, extractant, diluent, ultrasonic velocity, viscosity.

Introduction

In twenty first century the nuclear energy has already proven its importance as one of the major source of energy. Keeping in mind the very high energy needs and long term perspectives with limited nuclear fuel, it is of paramount importance to recover and reprocess spent nuclear fuel and rare earth elements from nuclear waste. Reprocessing consists of dissolution of spent nuclear fuel in acid medium and subsequent recovery of fissile materials and other actinides and lanthanide series of metals by standard solvent extraction technology. During reprocessing, there appear two distinct phases called organic phase, which contains the metal ion and an aqueous phase, which contains rest of the product. The emulsion phase, is termed as third phase which is called organo-aqueous phase, inhibits the phase separation and hence reduces the extraction efficiency. However, the third phase is eliminated by addition of a suitable blend of modifier/diluents to the extractant. In order to get that suitable blend the exact nature of interactions taking place between the modifiers and the diluents and/or extractant need to be known. Ultrasonic has high frequency which

makes it possible to obtain the information about molecular interactions between the molecules of the medium. The wavelength of this wave changes from one medium to another medium due to which it can be reflected off with very small surfaces and provides information from atomic/subatomic level. In addition to the high demand of clean energy, lanthanide elements as a group or as individual elements have wide applications in ceramics, lubricants, atomic energy, aero space, electronics, life sciences and many more. In the present work, Cerium oxide is taken as REE which is abundantly available in the earth crust along with other lanthanide elements in the mineral allanite bastanite, cerite *etc.* As a suitable extractant MIBK is used with toluene as diluents. Different acoustic properties have been studied with the help of propagation of ultrasonic wave at room temperature with different frequencies. The characteristic behaviour of the different acoustical parameters with their deviated values provides the information about nature of intermolecular interaction, which in turn helps in determining the suitable blend of the extractants and diluents for extraction of cerium oxide.

Materials and Methods

High purity and analytical grade samples of MIBK (AR> 98%), toluene (AR> 99 %), HNO₃ (AR>15.5 mol/L) and CeO₂ (AR> 99 %) procured from CDH Chemicals Pvt. Ltd., were used as received. The binary mixtures were prepared on percentage basis (w/w) by mixing known mass of toluene in appropriate masses of MIBK with the help of a high precision electronic balance of (WENSAR, PGB100, with accuracy ±0.001 gm). The ultrasonic velocity in the mixtures as well as in the component liquids were measured at 303.15 K (precise up to ± 0.01 m/s) by a single crystal variable path multifrequency ultrasonic interferometer operating at different frequencies 1 MHz - 4 MHz. The temperature of the mixture was maintained constant within ± 0.01 K by circulation of water from thermostatically regulated constant temperature water bath (B-206). Viscosities of the mixtures measured by Redwood apparatus were precise up to ±0.0001Ns.m⁻².

Preparation of Samples

Different concentrations of extractant were prepared by dissolving various amounts of MIBK in toluene. All samples were stored in ground-glass stopper bottles to prevent evaporation. For extraction, equal volumes of two phases, organic and aqueous phases were equilibrated in a separatory funnel by using magnetic stirrer at 200 rpm for 10 minutes as shown in Fig. 1.

Organic phase was equilibrated by adding MIBK with toluene of different mole fraction and aqueous phase was created by adding cerium oxide in diluted nitric acid using 25 ml flask. After this, the necessary volumes of both aqueous and organic phases were put into a separatory funnel, which was dipped in ultrasonic bath for phase settle. After the phase settle, the extract was filtered through Whatman filter paper No. 42. Mass balance

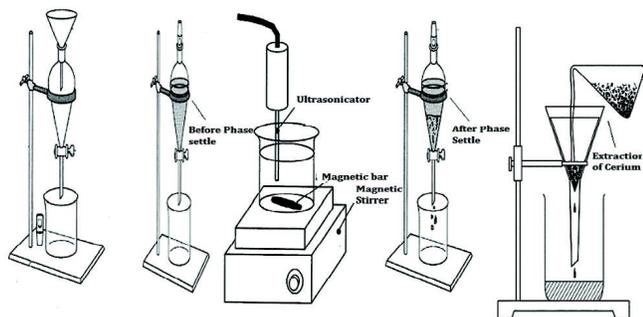


Fig. 1 Schematic diagram for extraction procedure of Ce from CeO₂

analysis was performed to verify the measured distribution ratios by comparing the theory of chemical equilibrium as per Nernst distribution law :

$$K_D = \frac{[X]_{org}}{[X]_{aqu}}$$

where the brackets denote the concentration of X in each phase at constant temperature (or the activity of X for non ideal solutions). By convention, the concentration extracted into organic and aqueous phase appears in the numerator and denominator of equation and the resulting value of KD is large, indicating a high degree of extraction from aqueous phase into organic phase. Conversely, if KD is small, less chemical X is transferred from aqueous phase into organic phase. If KD is equal to 1, equivalent concentrations exist in each phase.

Results and Discussion

The computed values of density, measured values of viscosity and ultrasonic velocity in the binary mixture were used to calculate the different acoustic parameters and their deviated values are shown in Fig. 2-5. Figure 4 shows the variation of ultrasonic velocity for different temperature with increasing mole fraction of MIBK.

For the system of MIBK and toluene under study, there is an increase in density at low concentration region for non polar solvents like toluene (Fig. 2). Increase in density with concentration is due to the shrinkage in the volume of the mixture. In other words, the increase in density may be interpreted to the structure-maker of the solvent due to the added polar solvent. In the case of MIBK/toluene mixture, there is found to be a continuous increase in the density of the solution with an increase

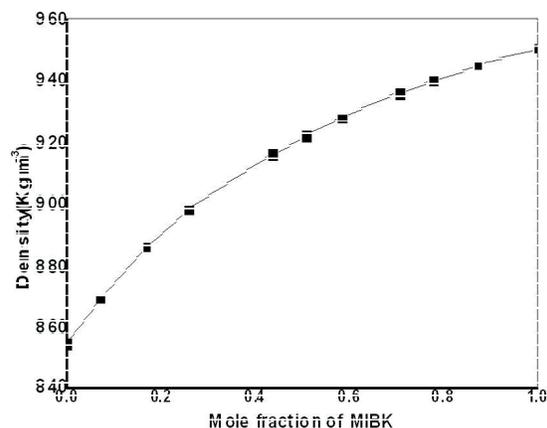


Fig. 2 Variation of density

in concentration of MIBK. This is attributed to the presence of strong intermolecular attraction such as dipole-dipole and dipole-induced dipole interaction¹⁻². The viscosity values are seen to follow a decreasing trend with the increase in the mole fraction of TBP in up to mole fraction 0.4 and then exhibit a steady increase with increase in concentration of TBP (Fig. 3) This kind of behaviour may be due to some agglomeration of complex formation occurring in the earlier stages, thereby causing a rise in the viscosity, which subsequently diminishes with increasing MIBK concentration. As the viscosity of MIBK is greater than that of toluene, its presence affects the viscosity of the mixture³.

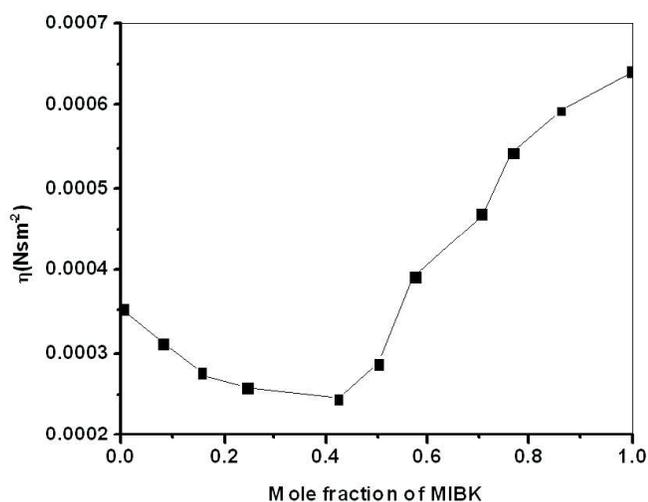


Fig. 3 Variation of viscosity

Figure 4 shows the variation of ultrasonic velocity in binary mixture of toluene with mole fraction of MIBK which is not linear. It is seen that the ultrasonic velocity

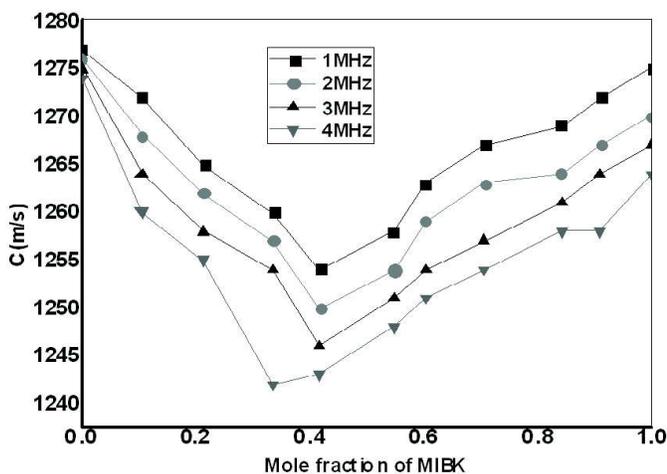


Fig. 4 Variation of ultrasonic velocity

decreases up to 0.4 mole fraction of MIBK and then increases with mole fraction of MIBK, depending on the ultrasonic velocity value of second component in the entire sample. The effect of adding a non-polar second component is primarily to disrupt the dipolar interactions of the first component. This may be due to self-association of the solvent molecules and a very weak dipole-induced dipole interaction between the component molecules, which is concentration dependent⁴.

From Fig. 5 it is observed that the excess molar volumes, V_m^E is negative which can be explained by the predominance of shrinkage in volume, caused by self association and difference in size and shape of component molecules, due to the dipole-dipole and dipole-induced dipole interactions⁵.

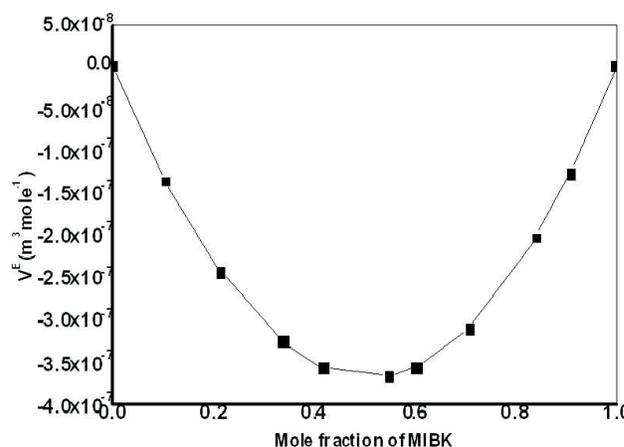


Fig. 5 Variation of Excess molar volume

In our study β_s^E and L_f^E is negative (Fig. 6 and Fig. 7) indicates that the solvent mixture is less compressible than the pure liquids forming the complex and molecules are more tightly bound than in pure liquids. This indicates the presence of relatively stronger molecular interaction, possible through hydrogen bonding⁶⁻⁷ between the component molecules. Mixing of MIBK with toluene will induce the breaking up of the associated clusters of MIBK releasing several dipoles which in turn can induce a dipole moment in toluene molecules, resulting dipole-induced dipole interactions. Thus, toluene acts as a structure breaker of MIBK. With the increase in frequency the interaction becomes weak and the breaking of associated structure of MIBK dominates, resulting in increase of β^{E8} . The negative values of L_f^E are attributed to close packaging of the component molecule decreases up to 0.4 mole fraction of MIBK and then increase

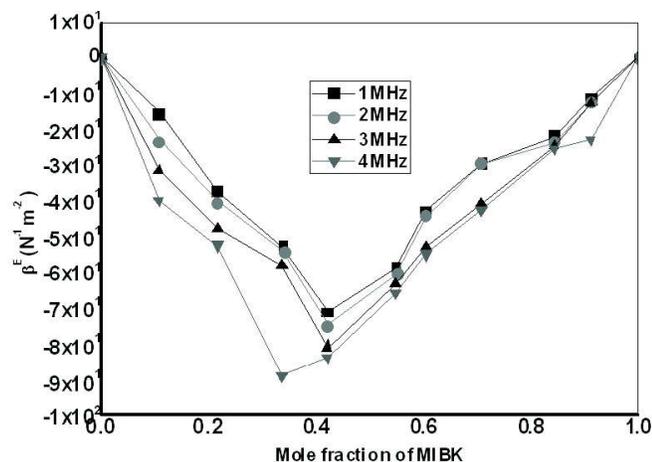


Fig. 6 Variation of excess adiabatic compressibility

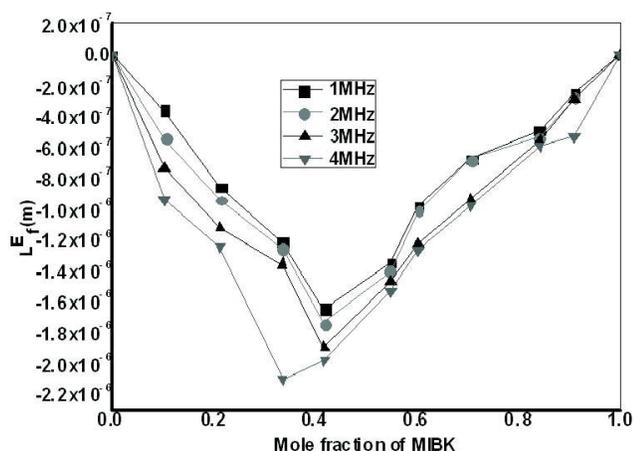


Fig. 7 Variation of excess intermolecular free length

negatively attributing to loose packing of the component molecules which in fact supports the heteromolecular association between the MIBK and toluene. This results the decrease in free length between the component molecules indicates that the system is more resistant to the sound propagation.

The negative excess acoustic impedance (Z^E) value indicates that over the concentration range of 0.3-0.4 mole % for MIBK significant interaction between the molecules of solvent is present as shown in Fig. 8. This is attributed due to interaction between component molecules and formation of closer molecular aggregates which leads to decrease in the intermolecular free space.

The intense discussion on physico chemical parameters of extractants and diluent makes it suitable for their compatibility up to a particular concentration (0.4 - 0.5

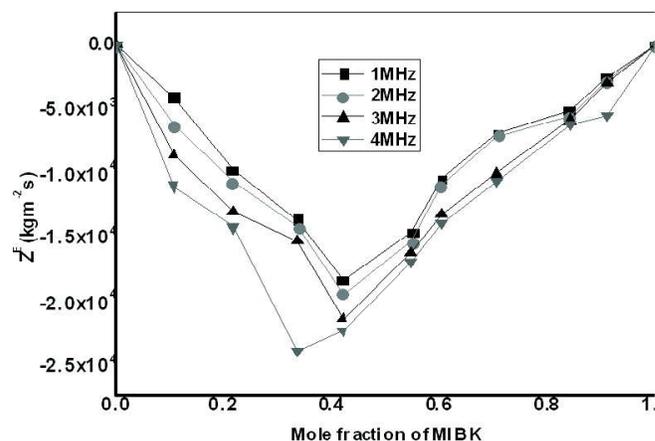


Fig. 8 Variation of excess acoustic impedance

mol %) as confirms from the variation of each physico chemical parameter. For the extraction process each concentration of MIBK/Toluene was treated with CeO_2 in addition of HNO_3 and the distribution coefficient recorded as per Nernst distribution law. The extraction of cerium increased steadily with an increase in MIBK concentration up to 0.5 mole fraction and then plateaued as shown in Fig. 9. Though diluent are unable to extract metal ion from the aqueous phase, but they greatly affect the extraction behaviour of extractants⁹.

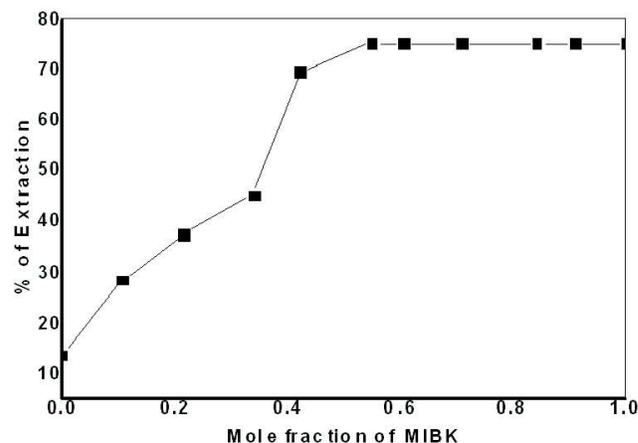


Fig. 9 % of extraction of Ce

Conclusion

The variation of density and viscosity and excess physico chemical parameter from certain concentration hints the presence of compatibility of the solvent mixture which explains the disappearance of the third phase interms of intermolecular interaction. Again the

extraction of cerium for each concentration of MIBK and toluene indicates the maximum efficiency of the MIBK and toluene is the same as demonstrated by each physico chemical parameter. The nature of interaction present in the MIBK and toluene mixture provides an optimized value for the extraction process. As such toluene with MIBK may be used as effective diluents/modifiers in the extraction of cerium from cerium oxide material.

Acknowledgements

The authors are thankful to Vice Chancellor, Veer Surendra Sai University of Technology for financial support to carry out the research work.

References

- 1 **Ali A., Nain A.K. and Kamil M.**, Physical-chemical studies of non-aqueous binary liquid mixtures at various temperatures, *Thermochim. Acta.*, **274** (1996) 209.
- 2 **Ali A. and Nain A.K.**, Ultrasonic study of molecular interactions in N, N-dimethylacetamide+ethanol binary mixtures at various temperatures, *Acoust. Lett.*, **19** (1996) 181.
- 3 **Tuck D.G.**, Viscosity measurement on the system nitric acid + tri-n-butyl phosphate, *Trans. Faraday Soc.*, **57** (1961) 1297.
- 4 **Kannappan A.N. and Rajendran V.**, Ultrasonic studies on carboxylic acids with amine in a polar Solvent, *Indian J. Phys.*, **65** (1991) 266.
- 5 **Petek A. and Dolecek V.**, Excess molar volumes of binary liquid mixtures of cyclohexane-carbon tetrachloride and toluene-benzene at various temperatures, *Acta Chim. Slov.* **45** (1998) 153-160.
- 6 **Ali A., Nain A.K., Sharma V.K. and Ahmad S.**, Study of molecular interaction in ternary mixtures through ultrasonic speed measurements, *Phys. Chem. Liq.*, **42** (2004) 375-383.
- 7 **De A.K., Khopkar S.M. and Chalmers R.A.**, *Solvent Extraction of Metals*. Van Nostrand, London, (1970).
- 8 **Nath G. and Paikaray R.**, Effect of frequency on acoustic parameters in a binary mixture of polar liquids, *Indian J. of Phys.*, **83** (2009) 1567-1574.
- 9 **Habashi F.**, *A Text book of hydrometallurgy*, Metallurgie Extractive Quebec", Enr, (1993).

Density and speed of sound of binary liquid systems in temperature range 288.15 to 318.15 K

Vivek Kumar Pundhir¹, V.S. Gangwar² and Rajeev Kumar Shukla^{2,*}

¹Department of Basic Sciences, Sagar Institute of Research & Technical Excellence, Bhopal-462041, India

²Department of Chemistry, V.S.S.D. College, Kanpur-208002, India

*E-mail: rajeevshukla47@rediffmail.com

Speed of sound for two binary systems (1-propanol and 2-propanol with n-dodecane) were computed at T= (298.15, 308.15, and 318.15) K over the whole composition range at atmospheric pressure by utilizing various theoretical models. Speed of Sound was fitted to Redlich-Kister polynomial equation to estimate the binary coefficients and standard errors. The theoretical models used in the computation were also tested for different systems showing that they provide fair agreement between theory and experiment. A considerable comparison has also been made to study the associational behavior and molecular interactions involved for these systems

Keywords: Sound velocity, molecular interactions.

Introduction

Molecular interactions occurring in a variety of liquid mixtures and solutions can be studied with the help of ultrasonic velocity. Extensive work has been carried out by many workers¹⁻² to investigate liquid state through analysis of ultrasonic propagation parameters and to correlate ultrasonic velocity with other physical and thermodynamic parameters. General applicability and comparison merits of the various models in binary solvent mixtures of aprotic protophobic solvent with aprotic protophilic solvents having distinctly different Gutmann donor numbers is the major object of the present work. As a part of research concerning the thermo chemical studies on new working fluid pair, we present here some useful data on speed of sound for three binary systems. These data were analyzed in terms of Ramaswamy and Anbananthan (RA) model⁴ model suggested by Glinski⁵ and Prigogine-Flory-Patterson (PFP) model⁶. The first two models, RA and model devised by Glinski (associated) are based on the association constant as adjustable parameters whereas PFP and others (non-associated) are based on the additivity of liquids. From these results, deviations in ultrasonic velocity, Δu were calculated and fitted to the Redlich-Kister polynomial equation⁶ to derive the binary coefficients and the

standard errors. An attempt has also been made to correlate the experimental data with the McAllister multi body interaction model⁷ which is based on Eyring's theory of absolute reaction rates.

Modeling

Ramaswamy and Anbananthan Model (RA Model)

Ramaswamy and Anbananthan proposed the model based on the assumption of linearity of acoustic impedance with the mole fraction of components. He assumed that when solute is added to solvent the molecules interact according to the equilibrium as:



where $[A]$ is amount of solvent and $[B]$ is amount of solute in the liquid mixture. By applying the condition of linearity in speed of sound with composition and considering the non-associated component present in the liquid mixture, eq takes the form,

$$u_{RA} = [x_A u_A + x_B u_B + x_{AB} u_{AB}] \quad (2)$$

where x_A , x_{AB} , u_A and u_{AB} and u_{obs} are the mole fraction of A, mole fraction of associate AB, ultrasonic velocity of A, ultrasonic velocity of associate AB and observed ultrasonic velocity respectively.

Model Devised by Glinski

On inspecting the results obtained from Ramaswamy and Anbananthan model, Glinski suggested the equation assuming additivity with the volume fraction, ϕ of the components, the refined version of Natta and Baccaredda model as,

$$u_{Glinski} = \frac{u_A u_B u_{AB}}{\phi_A u_B u_{AB} + \phi_B u_A u_{AB} + \phi_{AB} u_A u_B} \quad (3)$$

where u_{cal} is theoretical ultrasonic velocity, ϕ_A , ϕ_B are the volume fractions of component A and B and u_A , u_B and u_{AB} are the ultrasonic velocity of components A , B and AB .

Prigogine-Flory-Patterson Model

Flory and collaborators used the cell partition function of Hirschfelder and Eyring and a simple van der Waals energy-volume relation, by putting $m = 3$, $n \rightarrow \infty$ so that the Flory equations for the mixing functions and partial molar quantities may be obtained from the general corresponding states equations given by making this particular choice of (m, n) . Patterson *et al* have drawn attention to the close connection between the Flory theory and corresponding state theory of Prigogine employing a simple cell model of the liquid state. In order to extend corresponding state theory to deal with the surface tension, Patterson and Rastogi used the reduction parameters as,

$$\sigma^* = k^{1/3} P^{*2/3} T^{*1/3} \quad (4)$$

called the characteristic surface tension of the liquid. Here k is the Boltzmann constant. Paterson and Rastogi extended the simple cell model theory of the surface tension of spherical molecules by Prigogine and Saraga to the case of chain molecules. A segment experiences an increase in the configurational energy equal to $-M\tilde{U}(\tilde{V})$ due to the loss of a molar fraction, M , of its nearest neighbors at the surface while moving from the bulk phase to the surface phase. Its most suitable value ranges from 0.25 to 0.29. In the present case the value of M is taken as 0.29 throughout the calculation. Thus on the basis of Flory theory, surface tension and speed of sound of liquid mixture are related to the ultrasonic velocity by well-known and well tested relation of Auerbach⁹

$$\sigma = \sigma^* \tilde{\sigma}(\tilde{V}) \quad \text{and} \quad u_{PFP} = \left(\frac{\sigma}{6.3 \times 10^{-4} \rho} \right)^{2/3} \quad (5)$$

All the notations used in the above equations have their

usual significance as detailed out by Flory.

McAllister - three body model

Taking concept of additivity, McAllister derived an equation for three body interactions as;

$$\begin{aligned} \ln u = & x_1^3 \ln u_1 + 3x_1^2 x_2 \ln u_{12} + 3x_1 x_2 \ln u_{21} \\ & + x_2^3 \ln u_2 - \ln[x_1 + x_2 M_2 / M_1] + 3x_1^2 x_2 \ln[(2 + M_2 / M_1) / 3] \\ & + 3x_1 x_2^2 \ln[(1 + 2M_2 / M_1) / 3] + x_2^3 \ln[M_2 / M_1] \end{aligned} \quad (6)$$

McAllister -four body model

If there is much difference in size of two molecules then four body model approaches more nearly a 3-dimensional treatment. Again considering different interactions and their fraction of total occurrences, energy of activation may be written as sum of energy of activations of various interactions

$$\Delta G^* = x_1^4 \Delta G_1^* + 4x_1^3 x_2 \Delta G_{112}^* + 6x_1^2 x_2^2 \Delta G_{112}^* + 4x_1 x_2^3 \Delta G_{221}^* + x_2^4 \Delta G_2^* \quad (7)$$

by techniques entirely analogous to method given above, the following equation is derived;

$$\begin{aligned} \ln u_{mix} = & x_1^4 \ln u_1 + 4x_1^3 x_2 \ln u_{112} + 6x_1^2 x_2^2 \ln u_{1122} \\ & + 4x_1 x_2^3 \ln u_{222} + x_2^4 \ln u_2 - \ln(x_1 + x_2 M_2 / M_1) \\ & + 4x_1^3 x_2 \ln[(3 + M_2 / M_1) / 4] + 6x_1^2 x_2^2 \ln[(1 + M_2 / M_1) / 2] \\ & + 4x_1 x_2^3 \ln[(1 + 3M_2 / M_1) / 4] + x_2^4 \ln(M_2 / M_1) \end{aligned} \quad (8)$$

where u , x_1 , u_1 , M_1 , x_2 , u_2 and M_2 are the ultrasonic velocity of mixture, mole fraction, ultrasonic velocity and molecular weight of pure component 1 and 2 respectively. McAllister coefficients are adjustable parameters that are characteristic of the system.

Results and Discussion

Values of thermal expansion coefficient (α) and isothermal compressibility needed in the PFP model were obtained from the equation which have already been tested in many cases by us¹⁰. Calculations were performed on the experimental work of Yeh *et al.*¹¹.

The mixing function $\Delta\sigma$ can be represented mathematically by Redlich-Kister polynomial equation for correlating the experimental data as;

$$y = x_1(1 - x_1) \sum_{i=0}^p A_i (2x_1 - 1)^i \quad (9)$$

where y refers to deviation in ultrasonic velocity (Δu), x_1 is the mole fraction and A_i is the coefficient.

McAllister coefficients a , b , and c were calculated

using the least square procedure and the results of estimated parameters and standard deviation between the calculated and experimental values are presented in Table 2-3.

The absolute average percent deviations (AAPD) in ultrasonic velocity obtained from different models are provided in Table 4. It is observed that associated

processes provide fairly good results as compared to non-associated. Higher deviation values in PFP model can be explained as the model was developed for non-electrolyte γ -meric spherical chain molecules and the system under investigation have interacting and associating properties. Moreover, the expression used for the computation of α and β_T are also empirical in

Table 1 – Coefficient of Redlich- Kister equation and standard deviation for ultrasonic velocity of binary liquid mixtures at various temperatures.

T/K	A0	A1	A2	A3	Std dev	A0	A1	A2	A3	Std dev
	1-Butanol+n-Dodecane					2-Butanol+n-Dodecane				
288.15	-5.95	-2.26	-26.04	18.01	0.53	-6.78	0.86	-9.59	15.21	0.38
298.15	-14.41	-3.14	-26.22	14.54	0.45	-14.62	-6.63	-15.15	17.80	0.36
308.15	-22.89	-5.27	-26.97	13.79	0.40	-20.94	-12.52	-21.72	18.11	0.32
318.15	-31.39	-5.20	-22.78	2.65	0.23	-25.24	-15.15	-25.89	10.67	0.24

Table 2 – Parameters of McAllister 3 body interaction model and standard deviation for ultrasonic velocity of binary liquid mixture at various temperatures.

T/K	a	b	Std dev	a	b	Std dev
	1-Butanol+n-Dodecane			2-Butanol+n-Dodecane		
288.15k	709.10	969.36	0.74	700.07	963.29	1.17
298.15k	687.34	939.90	0.68	676.84	934.35	0.97
308.15k	665.82	910.90	0.60	653.99	905.78	0.74
318.15k	644.36	882.82	0.54	631.55	877.78	0.52

Table 3 – Parameters of McAllister 4 body interaction model and standard deviation for ultrasonic velocity of binary liquid mixture at various temperatures.

T/K	a	b	c	Std dev	a	b	c	Std dev
	1-Butanol+n-Dodecane				2-Butanol+n-Dodecane			
288.15k	1334.02	1322.44	1315.44	0.31	1317.00	1305.02	1311.26	0.44
298.15k	1294.01	1282.65	1275.35	0.30	1273.27	1266.25	1270.66	0.48
308.15k	1254.29	1243.67	1235.75	0.30	1229.76	1228.48	1230.41	0.48
318.15k	1215.21	1204.58	1197.64	0.24	1187.17	1190.67	1191.28	1.79

Table 4 – Average percentage deviation of ultrasonic velocities from Prigogine-Flory-Patterson (PFP), Ramaswami (RS), Glinski (GLI), Mcallister 3 body (Mc3) and Mcallister 4 body (Mc4) models.

T/K	U PFP	U RS	U GLI	U Mc3)	U(Mc4)	U PFP	U RS	U GLI	U(Mc3)	U(Mc4)
	1-Butanol+n-Dodecane					2-Butanol+n-Dodecane				
288.15	1.07	0.04	0.22	0.05	0.02	1.30	0.20	0.37	0.07	0.03
298.15	2.07	0.14	0.36	0.04	0.02	1.83	0.24	0.63	0.06	0.03
308.15	0.29	0.23	0.52	0.04	0.02	0.40	0.26	0.90	0.05	0.03
18.15	1.85	0.15	1.15	0.04	0.01	2.13	0.10	0.82	0.03	0.12

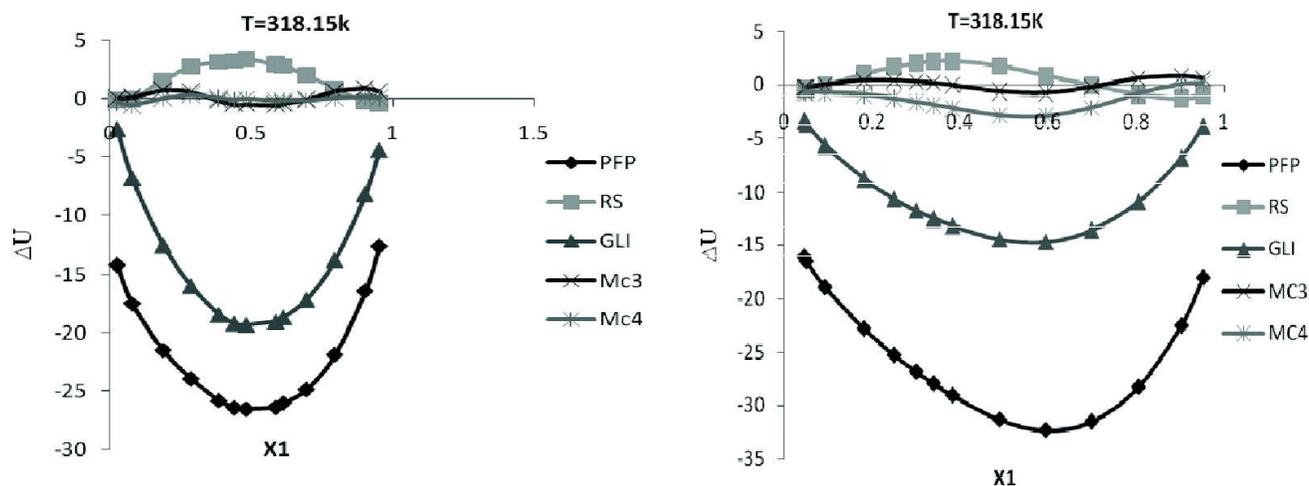


Fig. 1 Plot of ultrasonic velocity deviation ΔU with mole fraction for 1-Butanol + Dodecane and 2-Butanol + Dodecane at 318.15K.

nature. Positive deviations in speed of sound are a result of molecular association and complex formation whereas negative deviations are due to molecular dissociation. The actual sign and magnitude of deviations depend upon relative strength of two opposite effect. The lacks of smoothness in deviations are due to the interaction between the components molecules Results of ultrasonic velocity obtained from different models along with percent deviation are reported in Table 5. A careful perusal of the results clearly indicates the close proximity of our results with the experimental findings.

Plots of deviation in speed of sound obtained from various models with mole fractions at various temperatures are presented in figure1. In all the cases, minimum values of deviations in speed of sound are observed for associated models and maximum deviations are observed for non-associated, PFP model. The model suggested by Glinski provides better results as compared to Ramaswami and Anbananthan. The trend in all the figures is almost similar and negative which indicates stronger interactions between the liquid molecules.

Conclusion

Models assuming associated processes give more reliable results as compared to non-associated processes and helpful in deducing the internal structure of associates through the fitted values of ultrasonic velocity in a hypothetical pure associate and observed dependence of concentration on composition of a mixture.

References

- 1 **Satyanarayana G.R., Karuna Kumar D.B., Sujatha K., Khmanarao G. and Rambabu, C.**, Probing the intermolecular interactions in the binary liquid mixtures of o-chlorophenol with alkoxyethanols through ultrasonic, transport and FT-IR spectroscopic studies at different temperatures, *J. Molliq. Liq.* **216** (2016) 526-537.
- 2 **Klimaszewski Krzysztof., Lewkowska Ewa-Stronka., Trzcńska Ilona. and Bald Adam.**, Volumetric and acoustic studies on (tetraethylene glycol + water) mixtures in a wide temperature range. *J. Chem. Thermodyn.* **85** (2015) 191-201.
- 3 **Ebrahimi Nosaibah. and Sadeghi Rahmat.**, Volumetric and compressibility behaviour of poly(propylene glycol) - Amino acid aqueous solutions at different temperatures *J. Chem. Thermodyn.* **90** (2015) 129-139.
- 4 **Ramaswamy K. and Anbananthan D.**, Acustica. 1981, 48, 281-282, Determination of the conditional association constants from the sound velocity data in binary liquid mixtures. *J.Chem.Phy.* **118** (2003) 2301-2307.
- 5 **Glinski, J.** Determination of the conditional association constants from the sound velocity data in binary liquid mixtures ; *J. Chem. Phy.* **118**, (2003) 2301-2307.
- 6 **Abe A. and Flory P.J.**, The thermodynamic properties of mixtures of small non-polar molecules. *J.Am.Chem.Soc.* **82** (1965) 1838-1845 *J. Am. Chem. Soc.* 1965, **82** (1965) 1838-1845.
- 7 **Redlich O. and Kister A.T.**, Thermodynamics of nonelectrolytic solutions. Algebraic representation of

- thermodynamic properties and the classification of solutions. *Ind. Eng. Chem.* **40** (1948) 345-348.
- 8 **McAllister R.A.**, The viscosity of liquid mixtures, *AIChE J.* **6** (1960) 427-431
- 9 **Auerbach N.**, Correlation of Ultrasonic Velocity, *Experientia.* **4** (1948) 473
- 10 **Shukla R.K., Awasthi N., Kumar A., Shukla A. and Pandey V.K.**, Prediction of associational behaviour of binary liquid mixtures from viscosity data at 298.15, 303.15, 308.15 and 313.15 K, *J. Molliq. Liq.* **158** (2011) 131-138.
- 11 **Yeh Ching-Ta. and Hsiun Chein.**, Densities, Viscosities, Refractive Indexes, and Surface Tensions for Binary Mixtures of 2-Propanol + Benzyl Alcohol, + 2-Phenylethanol and Benzyl Alcohol + 2-Phenylethanol at T = (298.15, 308.15, and 318.15) K, *J.Chem. Eng. Data.* **52** (2007) 1760-1767

Acoustical parameters of binary mixture of pyridine and carbon tetrachloride

Dharamvir Singh Ahlawat^{1,*} and Mahipal Singh Gill²

¹Department of Physics, Chaudhary Devi Lal University, Sirsa- 125055, India

²Department of Physics, All India Jat Heroes Memorial College, Rohtak-124001, India

*E-mail: dahlawat66@gmail.com

The acoustical properties of a mixture of pyridine with CCl₄ have been carried out by ultrasonic technique at room temperature. The experimental data was used for the calculation of inter-molecular adiabatic compressibility, acoustic impedance and inter molecular free path length. The different type of molecular interactions in the mixture have also been discussed in the context of obtained acoustical parameters. Moreover, the change in the value of acoustic impedance with mole fractions of non-polar compound conclude that the interactions between dissimilar molecules are significant. It is also concluded that these interactions have a correlation with the polarizability of molecules in the compound mixture.

Keywords: Pyridine; CCl₄; molecular interactions; ultrasonic technique, acoustical parameters.

Introduction

Ultrasonic technique has been found to be a powerful method to characterize the physical behaviour of liquid mixtures and solid materials¹⁻³. During the last one decade a lot of work by this technique on binary and ternary liquid mixtures has been carried out by a number of research groups⁴⁻⁶. However, for the commercial use of this method in the industry more intensive research work is yet to be produced. The studies on volumetric, ultrasonic and viscometric properties of liquid mixtures and their dependence on composition and temperature are of immense importance in many fields of applied research and biological processes⁶. Moreover, the study on structural changes in the solvent and environmental effect on a molecule may also be estimated by this method.

Palani *et al.*⁶ have studied the acoustical properties of ternary mixtures at different temperatures using the ultrasonic technique. The ternary electrolytic mixtures at different temperatures have also been reported by Palani *et al.*⁵ in an another paper. The ultrasonic attenuation in TbP has been studied by Bhalla *et al.*³. Furthermore, the ultrasonic study of molecular interactions in two different binary liquid mixtures of acetone + CCl₄ and acetone+benzene have been carried

out by Kumar *et al.*⁴. In the present course of study, the liquid mixture of pyridine and carbon tetrachloride (CCl₄) has been considered. The pyridine is an important liquid which is being used currently in the extraction process for coal to analyse its compounds and in the manufacture of vitamin B₆ and other drugs⁷. In this paper, some acoustical parameters of the mixture were determined. Moreover, the type of the interactions between the existing molecules have also been discussed.

Materials and Methods

The studied samples of pyridine and CCl₄ were of analar grade. The samples were purified by usual laboratory methods. The boiling points of the liquid samples agree well with their values reported in the literature. The ultrasonic velocity of the binary mixture of CCl₄ with pyridine was measured at 300°K using a single crystal variable path fixed frequency ultrasonic interferometer⁴, operating at 2 MHz. The accuracy of the ultrasonic measurement in the interferometer was ± 0.001 m/s. The densities of the samples were measured by a 10 ml specific gravity bottle calibrated with deionized double distilled water. In order to minimize the error of measurement, many maxima of ultrasonic velocity were allowed to pass and their number n was

counted. As all the maxima were recorded with highest swing of the needle on the micrometer scale of the interferometer. The total distance d moved by the reflector of the interferometer cell is given by:

$$d = n\lambda/2 \quad (1)$$

where λ is the wave length of ultrasonic wave. The frequency of the inter ferrometer's crystal is accurately known as 2 MHz and it was used for the calculation of ultrasonic velocity.

Theoretical Considerations

The ultrasonic velocity is given by the relation:

$$u = v\lambda \quad (2)$$

Considering the measured values of ultrasonic velocity (u) and density (ρ) of the mixture under study, some acoustical and allied parameters may be computed with the help of the following expressions⁵:

Adiabatic compressibility (β);

$$\beta = \frac{1}{u^2\rho} \quad (3)$$

Free path length (L);

$$L = K\sqrt{\beta} \quad (4)$$

where K is the temperature dependent constant and its value is $(93.875 + 0.375 T) \times 10^{-8}$. The acoustic impedance (Z);

$$Z = u\rho \quad (5)$$

Results and Discussion

The polar molecules of pyridine interact with non-polar molecules of CCl_4 . The effect of adding a non-polar

compound is first disturbing the existing dipolar interactions of the polar molecules of pyridine. The nature of these interactions can be understood by ultrasonic velocity, density and acoustic impedance measurements for different mole fractions at constant temperature.

The obtained acoustical parameters of the mixture have been given in the Table 1. The measured values of ultrasonic velocity and density have been used for the calculations of adiabatic compressibility, inter molecular free path length and acoustic impedance of the mixture under study⁵. The plot of ultrasonic velocity against the mole fraction of CCl_4 in pyridine has been shown in the Fig. 1. The ultrasonic velocity decreases with the addition of mole fractions of CCl_4 in pyridine. This indicates that a new kind of physical process has started in the mixture by the addition of CCl_4 compound. This may be due to self association of the solvent molecules and a very weak type of attraction like dipole-induced dipole between the dissimilar molecules. The inference of this plot is that

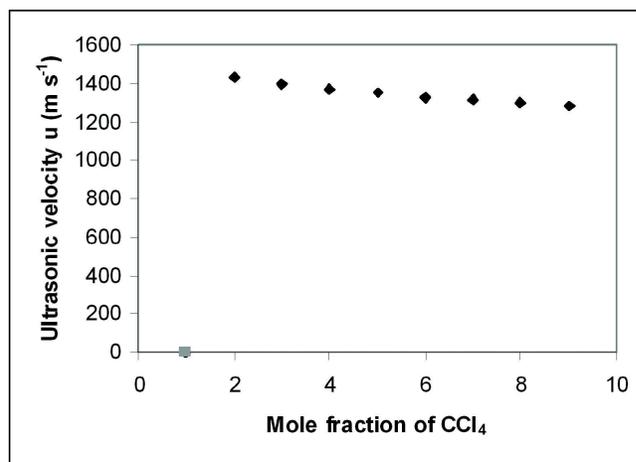


Fig. 1 Variation of ultrasonic velocity with mole fraction of CCl_4 .

Table 1 – Acoustical parameters of the mixture of pyridine with CCl_4

Ultrasonic velocity u (m s^{-1})	Mole fraction of CCl_4	Density of the solution ρ (kg m^{-3})	Acoustic impedance Z ($\text{kg m}^{-2} \text{s}^{-1}$)	Inter-molecular free path length 10^{-11} m
1430	0.050	852.42	1218.9×10^3	2.26
1400	0.150	870.67	1218.9×10^3	2.28
1370	0.275	880.00	1205.6×10^3	2.32
1350	0.376	909.90	1228.4×10^3	2.31
1330	0.500	930.50	1237.6×10^3	2.32
1320	0.650	951.31	1255.7×10^3	2.31
1300	0.627	965.20	1254.0×10^3	2.33
1280	0.924	980.00	1254.4×10^3	2.35

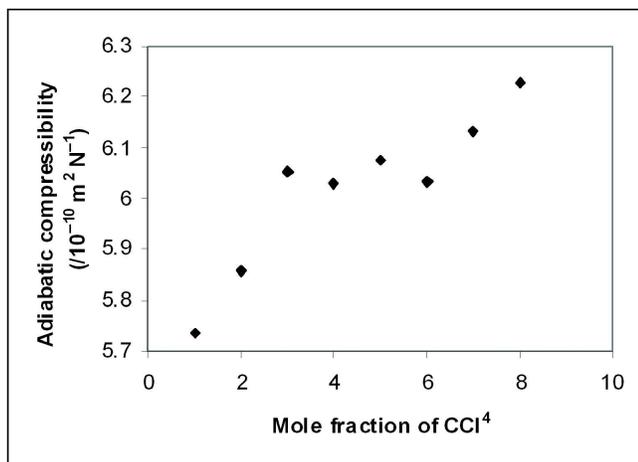


Fig. 2 Change in adiabatic compressibility with mole fraction of CCl₄.

the interaction is concentration dependent. A similar trend has been observed in the case of acetone and CCl₄ mixture by Kumar *et al.*⁴. The behaviour of adiabatic compressibility was observed as has been shown in the fig. 2. Since, the adiabatic compressibility with the change in concentration is the reverse of the trend of ultrasonic velocity and as it is inversely proportional to u^2 refer to Eq. (3).

This variation in adiabatic compressibility (β) values with concentration of CCl₄ indicate that the strength of induced dipole-induced dipole interactions is concentration dependent. These type of interactions are the weakest type. This increase in structural disorder of pyridine may result in more adhesion and leads to an increase in β . This increase in β results in a decrease in the value of ultrasonic velocity (u)⁸. The variation of intermolecular free path length with mole fraction of CCl₄ has been shown in the fig. 3. This parameter of the binary mixture may also be used for the discussion about the interaction between component molecules⁹. The increase of the intermolecular free path length with the increase in the concentration of CCl₄ in pyridine indicates that there is a weakening of intermolecular attractions between the molecules. This means that the concentration of dipole-dipole interactions due to polar molecules of pyridine decreases with the addition of CCl₄ as non-polar molecules.

The mixing of CCl₄ in pyridine may also be interpreted that CCl₄ molecules have induced the breaking up mechanism of the associated clusters of pyridine and thus there is a releasing of several dipoles. These released

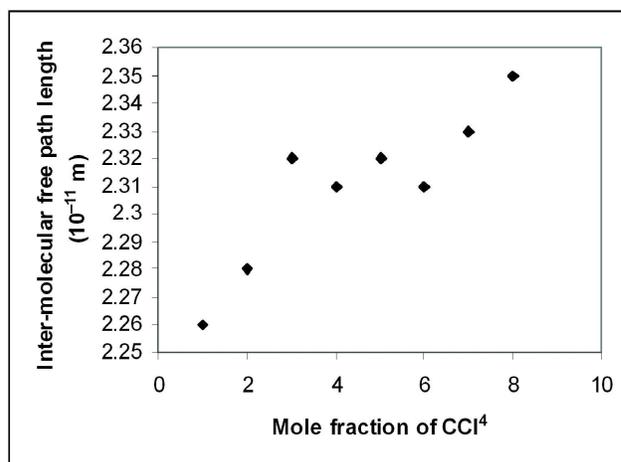


Fig. 3 Change in inter-molecular free path length with mole fraction of CCl₄.

dipoles can induce a dipole moment in CCl₄ molecules which results in the formation of dipole-induced dipole interactions in the mixture.

Conclusion

The change in ultrasonic velocity with mole fraction of the CCl₄ confirms the existence of molecular interactions between the existing molecules in the mixture. Moreover, the change in the value of acoustic impedance with mole fractions of non-polar compounds concludes that the interactions between dissimilar molecules are significant. The decrease in the strength of dipole-dipole attraction with the concentration of non-polar liquid may be manifested by the increase in intermolecular free path length. It is also concluded that these interactions have a correlation with the polarizability of the molecules in the compound mixture. Literature survey concludes that this technique is a simple, nondestructive and of low cost for the measurement of physical parameters of liquid and solid state mixtures.

References

- 1 **Rama Rao G.V., Vishwanatha Sarma A., Siva Ram Krishna J. and Ram Babu C.**, Theoretical evolution of ultrasonic velocities in binary liquid mixtures of o-chlorophenol at different, *Indian J. Pure Appl. Phys.*, **43** (2005) 345-354.
- 2 **Syal V.K., Chanhani S. and Kumari U.**, Ultrasonic velocity of binary mixtures of acetone and dioxane with dimethylsulphoxide as one component, *Indian J. Pure*

- Appl. Phys.*, **43** (2005) 844-848.
3. **Bhalla V., Singh D. and Jain S.K.**, Ultrasonic attenuation in terbium monophosphide, *J. Pure Appl. Ultrason.*, **38** (2017) 84-87.
 4. **Kumar R., Jaya Kumar S. and Kannappan V.**, Study of molecular interaction in binary liquid mixture, *Indian J. Pure Appl. Phys.*, **46** (2008) 169-175.
 5. **Palani R. and Jayachitra K.**, Ultrasonic study of ternary electrolytic mixtures at 303, 308 and 313K, *Indian J. Pure Appl. Phys.*, **46** (2008) 251-254.
 6. **Palani R. and Balakrishnan S.**, Acoustical properties of ternary mixtures of 1-alkanols in di-isopropyl ether and 2,2,2-trifluoroethanol mixed solvent, *Indian J. Pure Appl. Phys.*, **48** (2010) 644-650.
 7. **Arul G. and Palaniappan L.**, Ultrasonic study of 1-butanol in pyridine with benzene, *Indian J. Pure Appl. Phys.*, **43** (2005) 755-758.
 8. **S. Mullainathan and S. Nithiyathan**, Ultrasonic study of molecular interactions in binary mixtures at 303K, *E-J. Chem.*, **7**(2) (2010) 353-356.
 9. **Sathyanarayan B., Savitha Jyotsna T. and Satyanarayana N.**, Acoustic studies of binary mixtures of n-methylacetamide with some chloroethanes and chloroethenes at 308.15K, *Indian J. Pure Appl. Phys.*, **44** (2006) 587-591.

Characteristics of an ultrasonic array transmitter in the short range

Sahdev Kumar* and Hideo Furuhashi

Department of Electrical and Electronics Engineering, Aichi Institute of Technology,
1247, Yachigusa, Yakusa-Cho, Toyota, 470-0392, Japan.

*E-mail: kumarsahdev42@gmail.com

An ultrasonic array transmitter (12×12) has been developed and its theoretical studies were conducted in the short range. In the far field (>5 m), sound pressure level decreases exponentially with the distance. We have studied the effects of short pulse modulation on the array transmitter in the range from 0.5 m to 2 m to compare with our theoretical results. The sound pressure amplitude reduction in this region by $1/r$ does not follow the same as in the case of far field. The sound pressure level at 1 m was above 143 dB which can be considered to be useful for the biomedical applications. We also studied the normal reflected pulse from living and non-living object.

Keywords: Ultrasonic array transmitter, short range, pulse modulation.

Introduction

Ultrasonic transducers are known for non-contact presence and distance measuring applications based on the time of flight of echo¹⁻⁷. Properly selecting transducer's parameters influence the wave propagation characteristics. Therefore, phased array can be designed by analyzing the directivity patterns for their optimal uses. Ultrasonic sound in Nondestructive evaluation and Qualitative Nondestructive evaluation have the limitation due to a number of reasons such as high fabrication cost and complexity of the wave motion. An array can be used to perform different types of work based on the beam formation³. An ultrasonic sound source using 144 transmitting elements has been developed and its theoretical investigations on the directivity of different pattern of array transmitter were carried out with experimental confirmations^{8,9}. The effectiveness of an ultrasonic technique is greatly enhanced by the capability to focus the ultrasound. A conventional ultrasonic focused transducer is generally inflexible in the direction of ultrasonic radiation when it has fixed focal length. With the time delay, greater flexibility can be obtained which can generate a focal spot in the acoustic beam at a specified beam angle³⁻⁷. The main focus of this study was to observe the behavior of the ultrasonic array transmitter in the short range.

Theory

Continuous wave

First, we discuss the ultrasonic sound wave generated by the array transmitter for a continuous wave. A schematic block diagram of transmitting system is shown in Fig. 1. If a number of transmitting elements are positioned $P_i(x_p, y_p, 0)$ in xy plane toward the z axis (where $z=0$), then the total sound pressure from all of the elements is described Eq. (1) as follows¹⁰:

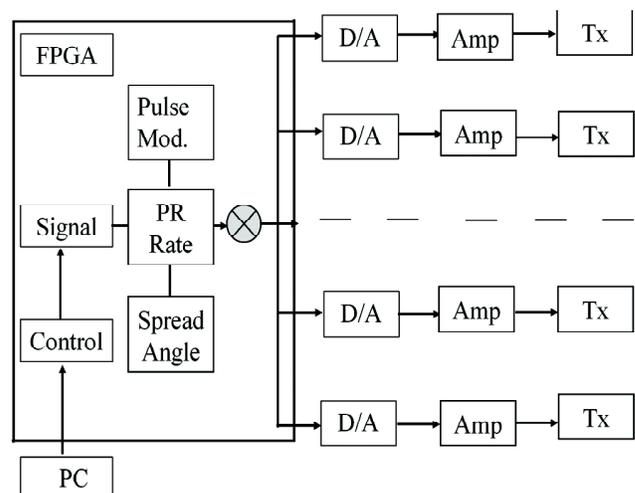


Fig. 1 A schematic diagram of the transmitting system.

$$p(x, y, z) = \sum_i D(\theta_i) A_i \frac{e^{-2\pi i \frac{r_i}{\lambda}}}{r_i} \quad (1)$$

Here, A_i is the amplitude of the sound pressure from one element, r_i is the distance between position P_i of the element and the observation point $P(x, y, z)$, θ_i is the angle between the z axis and the vector $\vec{P_iP}$, and $D(\theta_i)$ is the directivity of the circular transmitting element is given by Eq. (2) as follows^{8,9}:

$$D(\theta) = \frac{2J_1(ka \sin \theta)}{ka \sin \theta} \quad (2)$$

Here, θ is the direction of the sound wave, k is the wave number, a is the radius of an element, and J_1 is the Bessel function of the first kind. Here, absorption in air is not considered.

Figure 2 is a photograph of our developed ultrasonic array transmitter and Fig. 3 shows the coordinate system

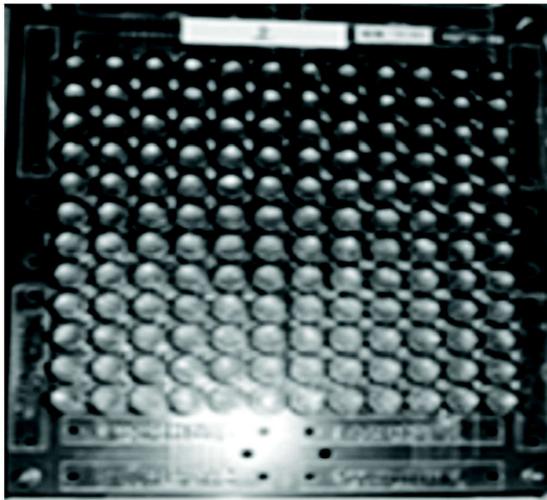


Fig. 2 A photograph of developed sound source.

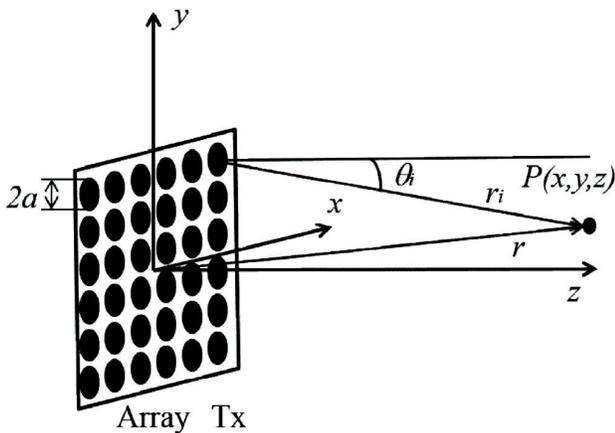


Fig. 3 A coordinate system of calculation.

for calculations. According to the transmission pattern of directivity, good interference among the sound waves is obtained in the area longer than 400 mm on the z axis. The interference in the area shorter than 400 mm is poor because different elements have different arrival times and different phases due to their different distances r_i . The farthest transmitter of the array is located 55 mm away from the center, therefore maximum phase difference is calculated by Eq. (3) as follows¹¹:

$$\Delta\phi = 2\pi \frac{\sqrt{\{(n-0.5)d\}^2 + z^2} - z}{\lambda} \quad (3)$$

Here, d is the interval of each element. If, on the z axis $(n - 0.5) d \ll z$, then

$$\Delta\phi \approx \pi \frac{\{(n-0.5)d\}^2}{\lambda z} \quad (4)$$

$$z \approx \frac{\pi \{(n-0.5)d\}^2}{\Delta\phi \lambda} \quad (5)$$

Therefore, the area in which good interference is obtained is calculated as follows from Eq.(5) using π for $\Delta\phi$ as shown in Eq. (6)

$$z_{interf} > \frac{\{(n-0.5)d\}^2}{\lambda} \quad (6)$$

Since $n= 12$ and $d=10$ mm in this case, the area in which good interference is obtained is calculated appx. 1.5 m.

Pulse modulation

This section discusses the influence of pulse modulation on the array transmitter. Ultrasonic range sensors work on the pulse echo method and it is assumed that sound amplitude is pulse modulated by Eq. (7) as follows^{8,9}:

$$A = A_0 e^{-\left(\frac{2t}{\tau}\right)^2} \quad (7)$$

Here, τ is the pulse width (half). The sound pressure at observation point, $P(x, y, z)$ is calculated by Eq. (8) as follows:

$$p(x, y, z) = \sum_i D(\theta_i) A_0 e^{-\left\{\frac{2(t-r_i/c)}{\tau}\right\}^2} \frac{e^{-2\pi i \frac{r_i}{\lambda}}}{r_i} \quad (8)$$

It is assumed that all transmitting elements have the same sound pressure amplitude. Wave velocity is denoted

by c , pulse width by τ . Time taken by the signal to reach to the sensor is t , λ is the wave length and r is the distance (from the center of array to the observation point). It is found that sound pressure does not increase linearly in far field as we increase the number of transmitting elements⁹.

Ultrasonic Array Transmitter

The beam directivity at an angle is quantified by the width of the lobe in that direction and is defined by the distance between the zero-crossing points of the lobe. Main lobe sharpness factor has a great influence on inter-element spacing. Therefore, ultrasonic array transmitter has been developed using 144 transmitting elements. All the elements are designed in the form of 12×12 arrays. A device T4010B4 transmitter is being used for transmission which has the resonant frequency of 40 kHz and beam width 100 degree (-6 dB full angle), maintaining inter element spacing 10 mm. A 40 kHz signal is modulated by 0.1 ms pulse with pulse repetition period of 400 ms in the short range. Signal is generated by field programmable gate array (FPGA) in the form of pulse width. The pulse width and pulse repetition period both are controlled by the personal computer. A D/A converter convert the generated signal into analog form, amplify it and sent it to transmitter for transmission. A device digital to analog converter (DAC) AD5415, which has large signal multiplying bandwidths of 10 MHz, has been used. These D/A convertors maintain the similar experimental conditions for each element signal after independent control of each transmitting element. All transducers are controlled by total four boards (one master board and three slave boards), so that same FPGA generated signal amplified equally before reaching to the transmitting element.

Experimental Set-up

The transmitted signal is received by a sensor as exhibited in Fig. 4.

The sensor is placed at 0.5, 1, 1.5 and 2 m apart from the transmitter. The transmitter and sensor both are on 1.5 m above the ground level and facing in opposite direction. The sensor is calibrated at the ultrasonic frequency by a system using a 1/4-inch free-field response microphone (46BE; frequency range 4 Hz-80 kHz, dynamic range 36 dB-157 dB, G.R.A.S Sound and Vibration A/S), a data acquisition module (USB-4431;

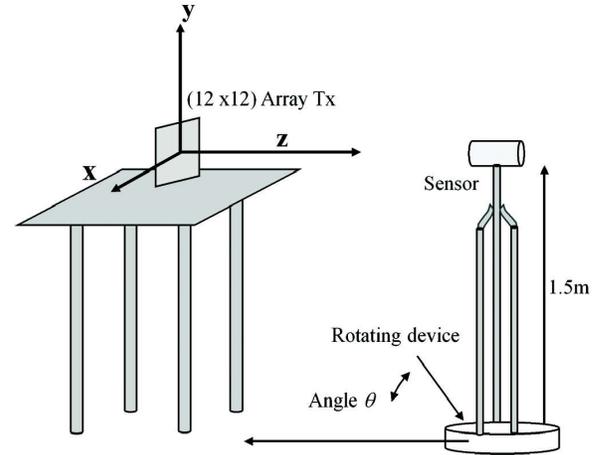


Fig. 4 Experimental setup.

24-Bit Analog I/O, sampling rate of 102.4 kS/s, National Instrument Corp.), and a sound measurement analyzer (NI Sound and Vibration Measurement Suite; National Instrument Corp.). A device MA40S4R (Murata Co. Ltd), is being used as a sensor which has a nominal frequency of 40 kHz and beam width of 80 degree. Maximum peak to peak voltage is measured, rotating the sensor on horizontal plane from 0 to 90 deg. at 2 deg. steps.

Results and Discussion

Figure 5 shows input vs output pulse width of array transmitter and single transmitter at different distances of the sensor.

An input pulse width 0.1 ms is applied to both the transmitter and its output is measured. This experiment

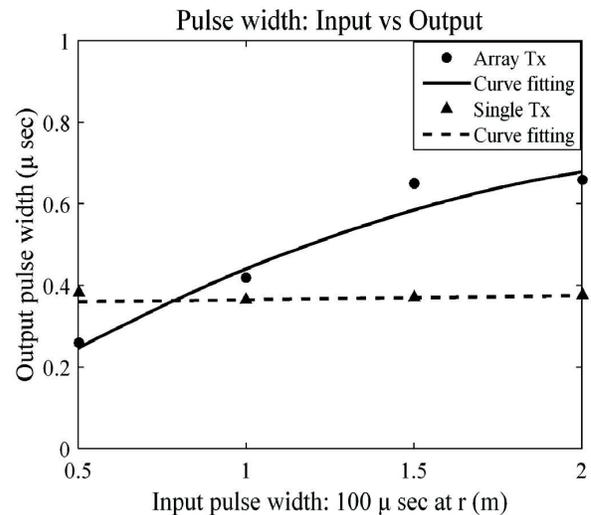


Fig. 5 Input vs Output pulse width: Array Tx and Single Tx.

was conducted in the region *i.e.* from 0.5 m - 2 m. Far field is considered beyond this region. Output pulse width does not show much variation when single transmitter is used. However, great difference in the output pulse width is observed using the array transmitter. Circles are the experimental results of the array transmitter and solid line is the curve fitting line. Triangles are the experimental results of the single transmitter and dashed line is curve fitting line.

Figure 6 shows the sound pressure level of both array transmitter and single transmitter.

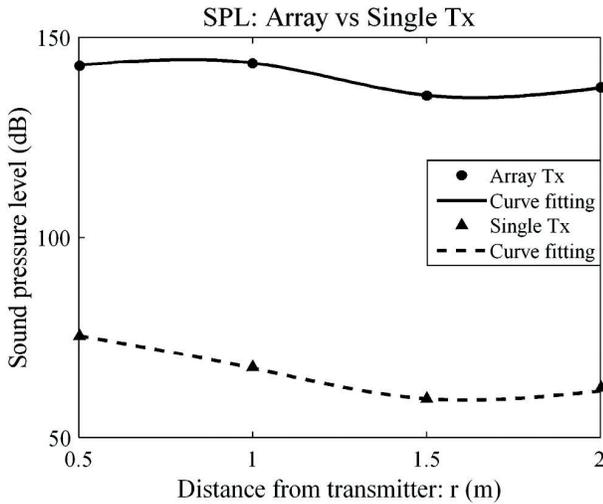


Fig. 6 Sound pressure level (Array Tx vs Single Tx).

Circles are the experimental results of the array transmitter and solid line is the curve fitting line. Triangles are the experimental results of single transmitter and dashed line is curve fitting line. Sound

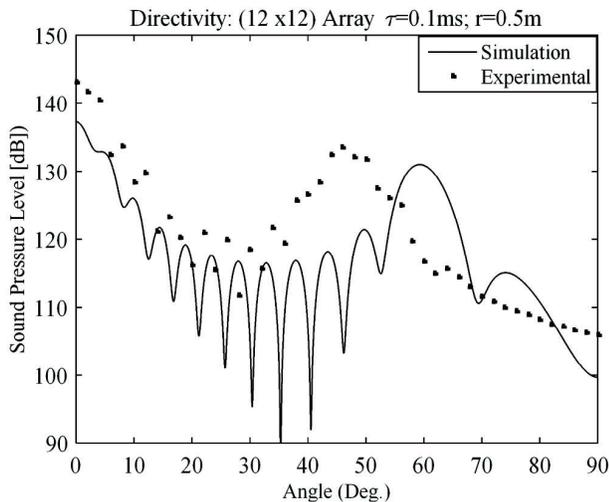


Fig. 7 Directivity: 0.1 ms and r=0.5 m.

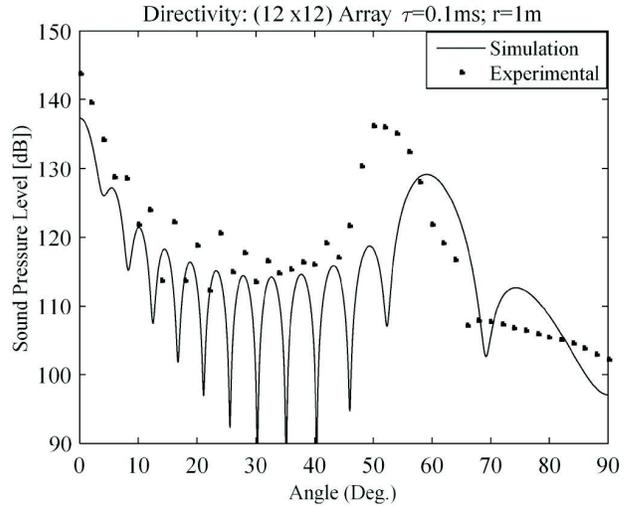


Fig. 8 Directivity: 0.1 ms and r=1 m.

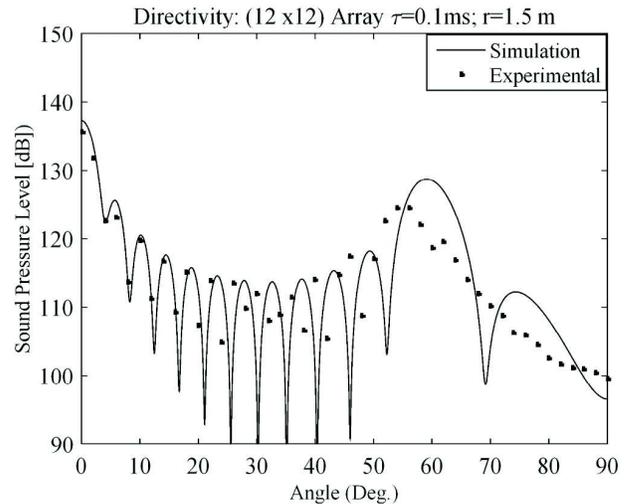


Fig. 9 Directivity: 0.1 ms and r=1.5 m.

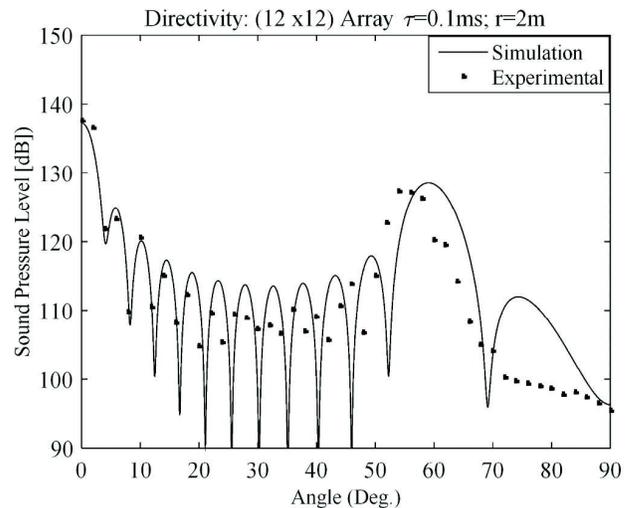


Fig. 10 Directivity: 0.1ms and r=2 m.

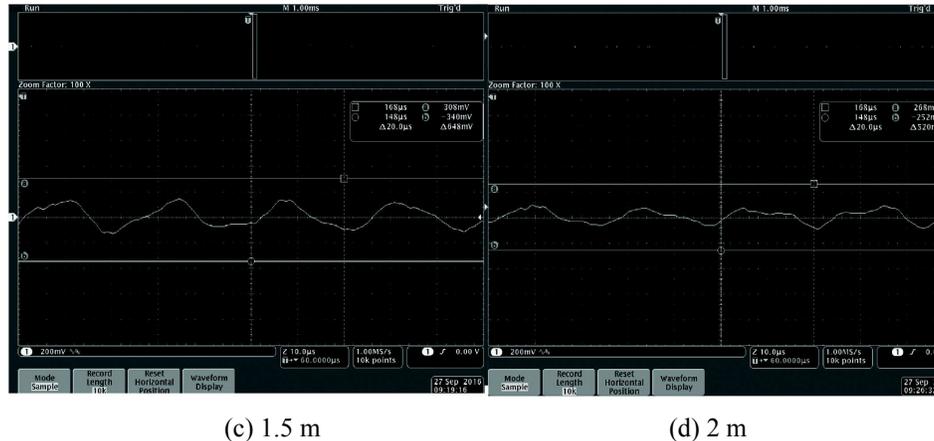


Fig. 12 Normal reflected signal of 0.1 ms pulse from palm at 0.5, 1, 1.5 and 2 m.

accurate, reliable and fast physically non-contact technique is required to avoid the human error for detecting the heart beats of effected person. The main purpose of this research was to study the behavior of the ultrasonic array transmitter in the short range.

Conclusion

An ultrasonic array transmitter was developed and investigated theoretically and experimentally. In the short range, air turbulence and absorption of ultrasonic wave is less and variation in sound pressure is also very less in the region (0.5 m - 2 m). Therefore, sound pressure increased n times where n is the number of transmitting element. Beyond this region sound pressure decreases conventionally as we increase the range. Sound pressure levels at 0.5 m, 1m, 1.5 m and 2 m has been obtained as 142.96 dB, 143.67 dB, 137.5 dB and 135.56 dB respectively. Sound pressure in the far field does not generate n times higher sound pressure using n transmitter elements. Less variation in the output pulse width is obtained when single transmitter is used but significant variation is found using array transmitter. When there is less variation in the pulse width, sound pressure level shows much variation and vice versa if there is more variation in the pulse width, sound pressure level shows less variation. Based on our array transmission system in the short range high sound pressure is maintained, that could be useful to distinguish the reflected pulse whether it is from living or non-living object in time domain. If it is possible then low cost, non-contact and accurate technique for biomedical applications can be developed, which would prove to be not only a boon to save many precious lives of human

beings and animals during causalities but also could be used for regular health check. Further experiments are in progress to confirm the feasibility of such biomedical applications and would be reported in our future publications.

Acknowledgements

The author gratefully acknowledges the fellowship received from Rotary Yoneyama Memorial foundation, Japan for this work, and also grateful to Prof. Masakazu Mori, Dr. Brahm Pal Singh and Ms. Aishwarya Singh for their valuable discussions/suggestions and experimental assistance.

References

- 1 Sato Y., Nakamoto M., Tamaki Y., Sasama T., Sakita I., Nakajima Y., Monden M. and Tamura S., Image guidance of breast cancer surgery using 3-D ultrasound images and augmented reality visualization. *IEEE Trans. Med. Imag.*, **17** (1998) 681-693.
- 2 Birkeland A., Solteszova V., Honigmann D., Gilja O.H., Brekke S., Ropinski T. and Viola I., The ultrasound visualization pipeline - A survey; URL: arXiv: 1206.3975v1 [cs.GR] 18 Jun 2012, pp.1-21.
- 3 Drinkwater B.W. and Wilcox P.D., Ultrasonic arrays for non-destructive evaluation: a review, *NDT & E International*, **39** (2006) 525-541.
- 4 Fink M., Time reversal of ultrasonic fields-part I: basic principles, *IEEE Transac. Ultrason. Ferroelect. Freq. Cont.*, **39** (1992) 555-566.
- 5 Wu F., Thomas J.L. and Fink M., Time reversal of

- ultrasonic fields-part II: experimental results, *IEEE Transac. Ultrason. Ferroelect. Freq. Cont.*, **39** (1992) 567-578.
- 6 **Cassereau D.** and **Fink M.**, Time reversal of ultrasonic fields-part III: theory of the closed time-reversal cavity, *IEEE Transac. Ultrason. Ferroelect. Freq. Cont.*, **39** (1992) 579-592.
 - 7 **Hickling R.** and **Marin S.P.**, The use of ultrasonics for gauging and proximity sensing in air, *J. Acoust. Soc. Am.*, **79** (1986) 1151-1160.
 - 8 **Kumar S.**, **Ichi K.** and **Furuhashi H.**, Theoretical investigation of high-power ultrasonic array transmitter for a range sensor in air, *Proc. of IEEE* DOI:10.1109/ICIT.2013.
 - 9 **Kumar S.**, **Wei Q.** and **Furuhashi H.**, Characteristics of high-power ultrasonic array transmitter in air, *Proc. IEEE 2015, Int. conf. on recent developments in control, automation and power engineering (RDCAPE 2015)*, 2015, pp.209-213. DOI:10.1109/RDCAPE.2015.7281397.
 - 10 **Kumar S.**, **Ichi K.** and **Furuhashi H.**, Theoretical investigation of the near field sound wave for an ultrasonic array transmitter, *Proc. Adv. Biomed. Eng.*, **14** (2012) 422-427.

PhD Thesis Summary

Ultrasonic Nondestructive Evaluation of Type 316 Austenitic Stainless Steel by Time-Frequency Analysis Methods

(Awarded 2014 by Homi Bhabha National University, Mumbai, to Dr. Govind Kumar Sharma, IGCAR, Kalpakkam)

The primary aim of the ultrasonic non-destructive investigations carried out in this thesis is to develop various time-frequency based signal processing methodologies to analyse ultrasonic signals for enhanced microstructural characterisation and imaging of defects in type 316 austenitic stainless steel. The time-frequency (TF) based signal processing techniques including short time Fourier transform (STFT), continuous wavelet transform (CWT) and Ensemble Empirical Mode Decomposition (EEMD) have been used. Specific software have been developed in LabVIEW and Matlab programming systems for accurate estimation of ultrasonic spectral parameters.

Specimens with a range of grain sizes (30-210 μm) were made by suitable heat treatments to the AISI type 316 austenitic stainless steel. The ultrasonic signals acquired from these specimens were analysed by time-frequency methods for microstructural characterisation. The understanding of frequency dependent attenuation is improved by using STFT and CWT analysis of these signals. The spectral information of the back-wall and backscatter could be obtained simultaneously by these approaches. Reliable peak frequency information could be obtained for back-wall echoes, even in the case of poor signal to noise ratio (SNR). The spectral information from back-wall echoes has been utilised for grain size characterisation. The STFT and CWT based time-frequency analysis techniques are established as useful tools for enhanced materials characterisation applications.

The application of time-frequency analysis techniques was extended to defect detection and imaging in coarse grain austenitic stainless steel. Specially designed coarse grained specimens with flat bottom holes (FBH) and side drilled holes (SDH) were made from suitably heat treated AISI type 316 stainless steel samples. The shift in the peak frequency of ultrasonic waves with propagation distance is measured by STFT approach. The ultrasonic signals obtained from artificial defects made at different depths were used for this purpose. The simultaneous availability of time and frequency information in STFT is utilised effectively. The systematic variation in the peak frequency with the

propagation distance has been validated by theoretical approach. The spectral information obtained at defect locations by STFT showed a definite range of frequencies for the defects at different depths. This information has been utilised to propose CWT based scheme for imaging of defects.

The wavelet based techniques require optimisation of mother wavelets and optimum selection of scales to reconstruct the signal. However, the recently proposed EEMD processing has the distinct advantage that it does not rely on a set of predefined basis functions and derives the basis functions from the signal itself, known as Intrinsic Mode Functions (IMFs). A novel adaptive signal processing methodology is proposed in this study for enhancing the signal to noise ratio of ultrasonic signals obtained from austenitic stainless steels of different grain sizes. The proposed method comprises of employing the signal minimisation algorithm to the IMFs obtained by Ensemble Empirical Mode decomposition (EEMD) of ultrasonic signals. It is possible to adaptively reconstruct the signal with enhanced signal to noise ratio based on a selected range of IMFs for a particular probe frequency. This proposed method works well for the range of grain sizes (30-210 μm) used in this study. The time-frequency based approaches used in the study provided better understanding of frequency dependent scattering in austenitic stainless steel. The limits imposed by conventional ultrasonic methods for grain size evaluation could also be extended by the proposed approaches. The shift in the peak frequency with propagation distances observed by the experimental results and mathematical model, paved the path for development of a single wavelet scale based CWT approach. This approach was used successfully for imaging of defects at various depths in thick coarse grain austenitic stainless specimens. The novel adaptive methodology proposed by employing signal minimisation algorithm on selected IMFs showed better than 15 dB enhancement in the SNR of the ultrasonic signals, can be used as a signal analysis approach for automatic detection of defects with improved sensitivity.

Journal of Pure and Applied Ultrasonics

(INDEXED IN: Indian Citation Index, Google Scholar, i-Scholar, UGC)

INFORMATION FOR AUTHORS

1. Type of Contribution

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.

Paper - These should be on original research work contributing to scientific developments. They should be written with a wide readership in mind and should emphasize the significance of the work.

Reviews and Articles - Includes critical reviews and survey articles.

Research and Technical notes - These should be short descriptions of new techniques, applications, instruments and components.

Letters to the editor - Letters will be published on points arising out of published articles and papers and on questions of opinion.

Miscellaneous - Miscellaneous contributions such as studies, interpretive and tutorial articles, conference reports and news items are also accepted. Recommended contribution lengths are: Papers 2000-4000 words. Reviews and Surveys 2000-5000 words; Conference Reports 500-1500 words; News Items, Research and Technical Notes up to 1000 words.

2. Manuscripts

Manuscripts should be typed on one side of the paper in double spacing with 25 mm margin on all sides of A4 size paper. A soft copy of the manuscript in MS

WORD for text and MS EXCEL for illustrations and a PDF file thereof may be sent by e-mail or CD/DVD. Colour images should be formatted as JPEG files. Figures submitted in colour would be published in colour. Colour should be avoided unless it is required in order to convey a message or serve a purpose in the image.

Title - Titles should be short and indicate the nature of the contribution.

Abstract - An abstract of 100-200 words should be provided on the title page of paper and review article. This should indicate the full scope of the contribution and include the principal conclusions.

Mathematics - Mathematical expressions should be arranged to occupy the minimum number of lines consistent with clarity e.g., $(x^2+y^2)/(x-y)^{1/2}$.

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

References - References should be referred to in the text by number only. The reference number should be given as superscript. The corresponding reference shall contain the following information in order; names and initials of author (s)(bold), title of the work, journal or book title (italic), volume number (bold), year of publication in brackets, page number, e.g., **Kumar S. and Furuhashi H.**, Anisotropic divergence controlled ultrasonic transmitter array for three dimensional range imaging, *J. Pure Appl. Ultrason.*, **38** (2016) 49-57.

Units and Abbreviations - Authors should use SI units wherever possible.