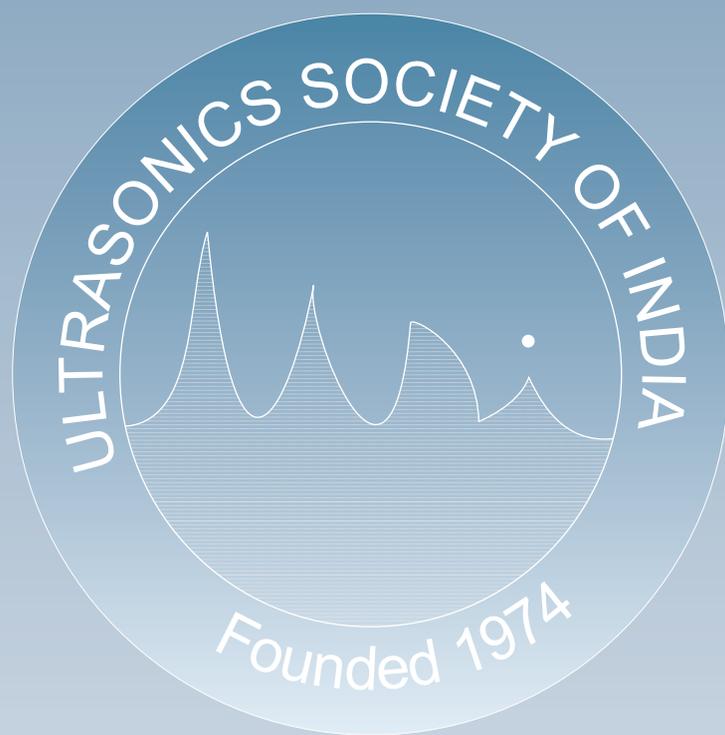


Journal of Pure and Applied
Ultrasonics



Website : www.ultrasonicsindia.org

A Publication of Ultrasonics Society of India



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. Yudhisther Kumar Yadav
kyadav6659@gmail.com

Joint Secretary Prof. O.P. Chimankar
opchimankar28@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
Dr. (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
poongodinagaraj@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. 2	Volume 40	April-June 2018
-------	-----------	-----------------

Chief Editor : Dr. S.K. Jain
Former Chief Scientist
CSIR-National Physical Laboratory, New Delhi
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 Vice-Chancellor, Veer Bahadur Singh Purvanchal
University, Jaunpur, U.P.

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. (Mrs.) Kirti Soni CSIR-National Physical Laboratory, New Delhi
Dr. (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, devices 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 40

NUMBER 2

APRIL-JUNE 2018

CONTENTS

Thermoacoustical and excess properties of binary mixtures poly (ethylene glycol) butyl ether (PEGBE) 206 with 1-butanol and 2-(methylamino) ethanol (MAE) Sudir Kumar, Sangeeta Sagar and Manisha Gupta	31
Synthesis and ultrasonic characterization of CuO-PVA nanofluids A. Mathana Gopal, A. Moses Ezhil Raj and J. Poongodi	39
Studies of ultrasonic and acoustic parameters of Cu (II) surfactant of fresh and treated sesame and soyabean oils at high temperature for different time Renu Bhutra, Rashmi Sharma and Arun Kumar Sharma	46
Comparative study of molecular interactions in ternary liquid mixtures by ultrasonic techniques Manoj Kumar Praharaj	52
Ultrasonic absorption of guanine in acidic solution P. D. Bageshwar, O. P. Chimankar and N. R. Pawar	57
Ph.D. Thesis Summary	60
Inauguration of USI Student Chapter- Thiagarajar College, Madurai	61
Forthcoming Events	62

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

Thermoacoustical and excess properties of binary mixtures poly (ethylene glycol) butyl ether (PEGBE) 206 with 1-butanol and 2-(methylamino) ethanol (MAE)

Sudir Kumar*, Sangeeta Sagar and Manisha Gupta

Department of Physics, University of Lucknow, Lucknow- 226007, India

*E-mail: sudhircbmr@gmail.com

In the view of the wide scope of experimental values of thermodynamical properties that allow us to establish new predictive interactions and information about the mixtures of Poly ethylene glycol butyl ether (PEGBE) 206 with 1-Butanol and 2-Methylamino ethanol (MAE) respectively, measurement of the thermophysical properties such as ultrasonic velocity, density and refractive index of binary over the whole composition range at 298.15 K, 303.15 K and 313.15 K under atmospheric pressure. To gain some insight into the molecular interactions present in these mixed solvents, thermodynamic parameters like polarisability, molar refraction, free volume, deviation in ultrasonic velocity, excess internal pressure and molar refraction deviation have been derived. The intermolecular interactions were discussed on the basis of the measured and the derived properties. The calculated excess values and deviation quantities been fitted to Redlich-Kister polynomial equation. The results were analyzed in terms of molecular interactions and mixing behavior between mixture components with taking into consideration effect of temperature.

Keywords: Ultrasonic velocity, polarisability, excess intermolecular free length, Redlich-Kister polynomial equation.

Introduction

Ultrasonic velocity in a medium is related to the binding forces between the molecules. Ultrasonic velocities in liquid mixtures consisting of polar and non-polar components are of considerable importance in understanding the intermolecular interaction between component molecules and find applications in several industrial and technological processes. Physical concept of liquid model states that in the liquid molecules are loosely packed and have some free space between them. The intermolecular free space and its dependent properties are related to intermolecular interactions and may reveal the information regarding the interaction, which may be occurring when the liquids are mixed together.

Ultrasonic spectroscopy is an excellent non-destructive technique for probing the structure of materials. The ultrasound waves when applied to liquids give information about molecular motion. This study is a powerful tool in characterizing the various aspects of

physico-chemical behavior of liquid mixture and studying the interaction between the liquid mixture¹⁻². The variation of ultrasonic velocity and related acoustical parameters throw much light upon the structural changes associated with the liquid mixtures having weak as well as strong interacting components³. The study and understanding of physico - chemical properties of liquid mixtures are important for applications in industries. Such studies in multicomponents (binary, ternary, quaternary etc) mixtures have been carried out by infra-red⁴, Raman⁵, nuclear magnetic resonance⁶, acoustica² and dielectric⁷ techniques. A measurement of ultrasonic velocity in the binary mixtures and solutions has been found to be an important tool to study the physico-chemical properties of mixtures.

In recent years, there has been considerable upsurge in the theoretical and experimental investigation of the excess thermodynamic properties of binary liquid mixtures⁸⁻⁹. Thus an attempt has been made to investigate the thermo physical properties of such mixtures.

Ultrasonic velocity (u_m), density (ρ_m) and refractive index (n_m) for the binary mixtures *viz.* Poly(ethylene glycol) butyl ether (PEGBE) 206 with 1-Butanol and 2-(Methylamino) ethanol (MAE) have been measured over the entire composition range at three temperatures $T=293.15$ K, 303.15 K, and 313.15 K, at atmospheric pressure. Polarisability (α), molar refraction (R_m), free volume (V_f), deviation in ultrasonic velocity (Δu), excess internal pressure (π_i^E) and molar refraction deviation (ΔR_m) have been computed from experimental data over the entire composite range at temperatures $T=293.15$ K, 303.15 K, 313.15 K. These excess parameters have been correlated with Redlich - Kister polynomial equation. The results have been interpreted on the basis of hydrogen bond formation and strength of intermolecular interaction occurring in these mixtures.

Experimental

Materials

Poly (ethylene glycol) butyl ether (PEGBE) - 206, 2-(Methylamino) ethanol (MAE) (98.5%) and 1-butanol (99%) were obtained from Sigma-Aldrich Chemicals Ltd. and no further purification was done. Purity of these compounds has been compared with the literature data and is found to be in good agreement as shown in table 1. Structure of monomer of PEGBE is shown in Fig. 1.

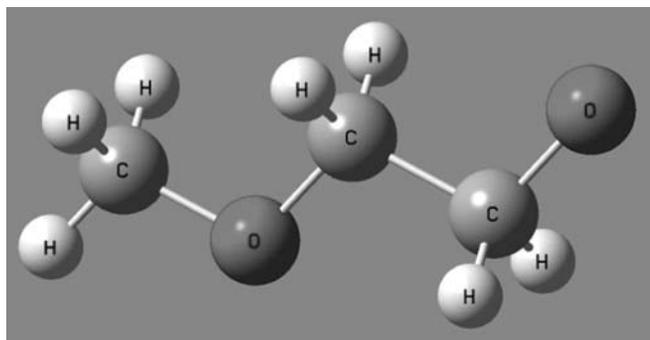


Fig. 1 Structure of monomer of PEGBE 206

Apparatus and Procedures

Mixtures were prepared by weighing the liquids in specially designed ground glass stoppered weighing bottles, taking extreme precautions to minimize preferential evaporation. An OHAUS (AR2140), USA single pan balance having a stated precision of 0.1 mg was used throughout. The maximum possible error in the mole fraction is estimated to be ± 0.0001 .

The ultrasonic velocity of the pure components and their mixtures were measured with a variable path, fixed frequency interferometer. It consists of a high frequency generator, a measuring cell, and digital display micrometer. This interferometer measures the ultrasonic velocity of liquids by determining the wavelength of ultrasonic pulses over the distance within the sample using a digital display micrometer. Measurements of ultrasonic velocity were made at a fixed frequency of 2 MHz. The calibration of the ultrasonic interferometer was done by measuring the velocity in AR grade benzene and CCl_4 with an accuracy of 0.08% . The experiments were replicated at least 5 times for each sample and the results reported are the average values.

Densities have been measured by a single capillary calibrated pycnometer made of Borosil glass, with a bulb capacity of 6.7 ml volume. The pycnometer stem contained graduation of 0.01 ml. Pycnometer was immersed vertically in a double walled cylindrical water circulated glass jacket. The positions of the liquid level were recorded with the help of travelling microscope (having a least count of 0.001 cm). The precision of the measured densities is of the order of $\pm 1 \times 10^{-4}$ g cm^{-3} . The average of four to five measurements was taken for each sample mixtures.

The viscosities have been measured using Brookfield LVDV-II + Pro Programmable cone and plate viscometer. The experimental assembly allows measurement of viscosities in the range of 0.15 cP to 3065 cP (with spindle CPE-40) and 4.6 cP to $92,130$ cP (with spindle CPE-52) with an accuracy of $\pm 1.0\%$ of full scale range and repeatability of $\pm 0.2\%$. The apparatus requires only 0.5 ml of the mixture for measurement of viscosity. The apparatus measures fluid absolute viscosity directly in cP. The apparatus was calibrated by two viscosity standards Polydimethyl siloxane with viscosity 4.6 and 485 cP. The viscosity standards are Newtonian, and therefore, have the same viscosity regardless to the spindle speed.

The refractive indices of the liquid mixtures under investigation have been measured using a thermostatic Abbe's refractometer which works with the wavelength corresponding to the D-line of sodium. The apparatus measures refractive indices in the range of 1.300 to 1.700 with an accuracy of ± 0.001 unit. An average of five measurements was taken for each sample mixture.

Circulating water bath with programmable temperature controller having variable pump speeds, has been used for water circulation in water jackets of the apparatuses. The temperature controller covers the temperature measurement range of -20°C to 200°C , with temperature stability of $\pm 0.01^{\circ}\text{C}$.

Results and Discussion

Experimental data

The experimentally measured values of ultrasonic velocities and densities for the systems PEGBE 206 + MAE and PEGBE 206 + 1-Butanol at 293.15 K, 303.15 K and 313.15K in whole composition rang are reported in Table 2.

Derived Parameters

For calculating polarisability (α), molar refraction (R_m) and free volume (V_f) following relations were used

$$\alpha = \frac{3 R_m}{4 \pi N} \quad (1)$$

$$R_m = \frac{n^2 - 1}{n^2 + 2} \quad (2)$$

$$V_f = \left[\frac{Mu}{k\eta} \right]^{\frac{1}{2}} \quad (3)$$

where ρ is the density, u is the ultrasonic velocity, η is the viscosity, M is the effective molecular mass, k is a dimensionless temperature-independent constant having a value of 4.28×10^9 .

The variation of free volume (V_f) with mole fraction of PEGBE 206 for the systems PEGBE 206 + MAE and PEGBE 206 + 1-Butanol is shown in Fig. 2. The graphical representation of free volume shows that for the system PEGBE 206 + 1-Butanol values of V_f are lesser than the pure components giving the minimum around $x = 0.1$ to 0.3. The non-linear behaviour of V_f reflects the complex formation at concentration through hydrogen bonding.

The values of molar refraction (R_m) and polarizability (α) are listed in Table 3. A close perusal of Table 3 reveals that the molar refraction values increases considerably on increasing the concentration PEGBE 206 for both the systems at all temperatures.

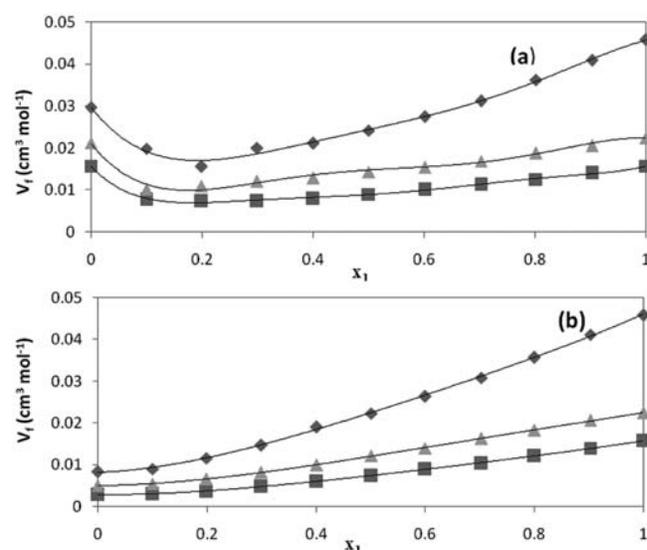


Fig. 2 Free volume for the systems (a) PEGBE + 1-butanol and (b) PEGBE + MAE at \blacksquare , 293.15; \blacktriangle , 303.15; and \blacklozenge , 313.15K with respect of the mole fraction of PEGBE.

Table 1 – Comparison of ultrasonic velocity (u), density (ρ) and refractive index (n) with literature data at different temperatures.

Component	T (K)	Unit ms^{-1} (u)		Unit $\times 10^3 \text{ kg m}^{-3}$ (ρ)		Refractive index (n)	
		Observed	Literature	Observed	Literature	Observed	Literature
PEGBE 206	293.15	1548.4	--	1.0047	--	1.444	--
	303.15	1516.0	--	0.9861	--	1.440	--
	313.15	1500.2	--	0.9785	--	1.436	--
MAE	293.15	1440.0	--	0.9401	--	1.440	1.4393
	303.15	1416.8	--	0.9328	0.9337 _e	1.435	1.4356 _d
	313.15	1399.2	--	0.9263	0.9259 _e	1.431	1.4318 _d
1-Butanol	293.15	1258.0	1256 _c	0.8097	0.8098 _a	1.397	1.399a
	303.15	1224.0	--	0.802	0.8017 _a	1.393	1.392a
	313.15	1195.0	1193 _b	0.7945	0.7934 _a	1.389	1.389a

^aRef.¹⁰, ^bRef.¹¹, ^cRef.¹², ^dRef.¹³.

Table 2 – Experimental values of ultrasonic velocity (u_m), density (ρ_m) and refractive index (n_m) for the systems PEGBE 206 + MAE and PEGBE 206 + 1-Butanol with respect to the mole fraction x_1 of PEGBE 206.

PEGBE 206+MAE				PEGBE 206 +1-butanol			
x_1	u_m /(ms ⁻¹)	ρ_m /(gm.cm ⁻³)	n_m	x_1	u_m /(ms ⁻¹)	ρ_m /(gcm ⁻³)	n_m
293.15K				293.15K			
0.0000	1452.0	0.9401	1.440	0.0000	1258.0	0.8097	1.397
0.1986	1486.5	0.9671	1.442	0.1989	1345.3	0.8953	1.435
0.4000	1514.8	0.9857	1.442	0.4000	1418.6	0.9576	1.441
0.5994	1530.0	0.9952	1.443	0.6007	1474.4	0.9843	1.441
0.7990	1538.4	0.9999	1.443	0.8018	1526.5	0.9998	1.443
1.0000	1548.4	1.0047	1.444	1.0000	1548.4	1.0047	1.444
303.15K				303.15K			
0.0000	1416.8	0.9328	1.435	0.0000	1224.0	0.8020	1.393
0.1986	1458.8	0.9582	1.438	0.1989	1330.5	0.8762	1.425
0.4000	1484.8	0.9728	1.438	0.4000	1400.6	0.9309	1.435
0.5994	1500.6	0.9808	1.439	0.6007	1456.0	0.9608	1.438
0.799	1510.4	0.984	1.439	0.8018	1498.3	0.981	1.441
1.0000	1516.0	0.9861	1.440	1.0000	1516.0	0.9860	1.440
313.15K				313.15K			
0.0000	1399.2	0.9263	1.431	0.0000	1195.2	0.7945	1.389
0.1986	1446.6	0.9513	1.434	0.1989	1308.8	0.8737	1.425
0.4.000	1472.5	0.9653	1.434	0.4000	1390.5	0.9243	1.429
0.5994	1486.2	0.9728	1.435	0.6007	1448.8	0.9509	1.434
0.799	1495.7	0.9771	1.435	0.8018	1484.2	0.9726	1.436
1.0000	1500.2	0.9785	1.436	1.0000	1500.2	0.9785	1.436

Polarizability (α) decreases with increase in the mole fraction of PEGBE 206 but increases slightly with increase in temperature for both the systems PEGBE 206 + MAE and PEGBE 206 +1-Butanol. This small effect of temperature might be due to small permanent electric dipole moments of the components and their mixtures, as orientation of molecular dipole is slightly disturbed by temperature.

Excess parameters

Excess parameters play a vital role in assessing the compactness due to molecular arrangement and the extent of molecular interaction in the liquid mixtures through charge transfer, dipole-dipole and dipole- induced dipole interactions. The sign and the extent of deviation of these functions from ideality depend on the strength of interactions between unlike molecules.

Deviation in ultrasonic velocity (Δu), excess internal pressure (π_1^E) and molar refraction deviation (ΔR_m) for the binary mixtures under study have been shown in Figs. 3-6. The excess parameters have been evaluated using following relations,

$$\Delta u = u_m - (x_1 u_1 + x_2 u_2) \quad (4)$$

$$\Delta R_m = R_m^{\text{expt}} - R_m^{\text{id}} \quad (5)$$

where $R_m^{\text{expt}} = \left(\frac{n_m^2 - 1}{n_m^2 + 2} \right) \left(\frac{x_1 M_1 + x_2 M_2}{\rho_m} \right)$ and

$$R_m^{\text{id}} = \left[\left(\frac{n_1^2 - 1}{n_1^2 + 2} \right) \frac{M_1}{\rho_1} \phi_1 + \left(\frac{n_2^2 - 1}{n_2^2 + 2} \right) \frac{M_2}{\rho_2} \phi_2 \right]$$

$$\pi_{im}^E = \frac{bRTk^{\frac{1}{2}} \eta_m^{\frac{1}{2}} \rho_m^{\frac{2}{3}}}{u_m^{\frac{1}{2}} M^{\frac{7}{6}}} - \left(\frac{x_1 bRTk^{\frac{1}{2}} \eta_1^{\frac{1}{2}} \rho_1^{\frac{2}{3}}}{u_1^{\frac{1}{2}} M^{\frac{7}{6}}} + \frac{x_2 bRTk^{\frac{1}{2}} \eta_2^{\frac{1}{2}} \rho_2^{\frac{2}{3}}}{u_2^{\frac{1}{2}} M^{\frac{7}{6}}} \right) \quad (6)$$

where $M_1, M_2; \rho_1, \rho_2, u_1, u_2; \eta_1, \eta_2;$ and $\phi_1, \phi_2;$ denote molecular weight, density, ultrasonic velocity, viscosity and volume fraction respectively of the pure components. ρ_m, u_m and η_m represent density, ultrasonic velocity and viscosity of the mixtures respectively. K, R, T and k denote Jacobson constant, gas constant, absolute temperature and dimensionless temperature independent constant having a value of 4.28×10^9 .

The sign and magnitude of excess molar volume changes that takes place on mixing is the result of several effects that can operate in the same or in the opposite direction.

Table 3 – Molar Refraction (R_m) and Polarizability (α) for the systems PEGBE + MAE and PPGMBE + 1-butanol with respect to the mole fraction x_1 of PEGBE.

PEGBE+MAE			PEGBE+1-BUTANOL		
x_1	R_m ($\text{cm}^3 \text{mol}^{-1}$)	α	x_1	R_m ($\text{cm}^3 \text{mol}^{-1}$)	α
	293.15K			293.15K	
0.0000	21.0556	0.001070	0.0000	22.0442	0.001217
0.2988	30.9277	0.001045	0.2988	32.2300	0.001107
0.5994	40.9228	0.001030	0.6007	41.2017	0.001053
1.0000	54.4608	0.001020	1.0000	54.4608	0.001021
	303.15K			303.15K	
0.0000	21.0103	0.001092	0.0000	22.0572	0.001237
0.2988	31.0506	0.001059	0.2988	32.3696	0.001128
0.5994	41.2196	0.001045	0.6007	41.9327	0.001066
1.0000	55.0611	0.001038	1.0000	55.0611	0.001038
	313.15K			313.15K	
0.0000	20.9872	0.001101	0.0000	22.0642	0.001256
0.2988	31.0466	0.001067	0.2988	32.3361	0.001136
0.5994	41.2045	0.001053	0.6007	41.9912	0.001079
1.0000	55.0420	0.001046	1.0000	55.0420	0.001046

The factors that are responsible for positive excess molar volume are :

- Disruption of one or both components during of mixing process, for example the rupture of H-bonding of one of the component by other, or by breaking up of association compound such as alcohols.
- Unfavorable fitting of molecules with each other due to the geometry of molecular structure.
- Existence of steric hindrance between the components of solutions.

The negative V_m^E arises due to the following factors:

- Existence of chemical interaction between unlike molecules such as hydrogen bond formation that makes the contraction of solution volume.
- Formation of weaker forces such as dipolar forces in the mixing process
- Accommodation of molecules of one component in to the structural space of other component or favorable fitting of constituent molecules.

A plausible qualitative interpretation of the behavior of these mixtures with composition has been suggested. The observed negative values of V_m^E can be ascribed by favorable interactions such as strong hydrogen bond, between hydroxyl group (-OH) of 1-Butanol and (-NH₂) of MAE (Fig. 3). The structural contributions arising

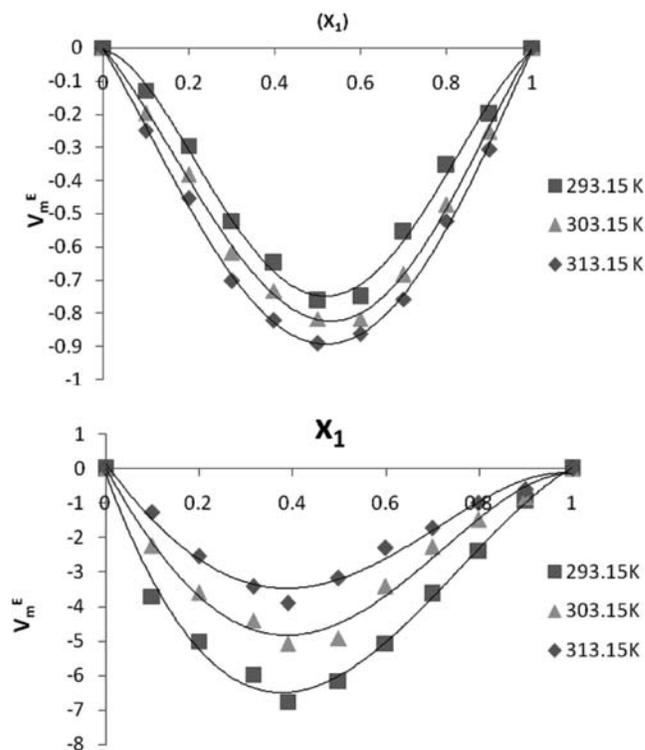


Fig. 3 Excess molar volume (V_m^E) versus the mole fraction of PEGBE 206 (x_1) for binary mixtures: (a) PEGBE 206 +MAE and (b) PEGBE 206 + 1-Butanol at 293.15K, 303.15K, and 313.15K.

from the geometrical fitting (interstitial accommodation) of one component into other due to the differences in

the free volume and the molar volumes between components leads to negative contribution to V_m^E . The actual value of V_m^E would depend on the relative strength of these effects. The experimental values of V_m^E suggest that H-bonding and interstitial accommodation both are leading to negative values with temperature suggest that structural effect is more predominant than chemical effect in these solutions because of the large differences in molar volume between components (molar volumes of PEGBE 206, MAE and 1-Butanol are 205.0249, 79.8922 and 91.5287 cm³ mol⁻¹ respectively, at 293.15K).

Figure 4 shows the deviation in ultrasonic velocity (Δu) is positive and increases with a rise in temperature for both the system, the deviation in ultrasonic velocity is more positive for the system PEGBE 206 + 1-Butanol as compared to the system PEGBE 206 + MAE. These kinds of variation suggest that significant interactions are present in these mixtures. The sign and magnitude of deviation in ultrasonic velocity plays an important role in describing molecular arrangements as a result of specific interactions occurring in the liquid mixture. In general positive deviation in ultrasonic velocity indicate the presence of significant interactions and negative deviations in ultrasonic velocity indicate the weak interactions between the unlike molecules. Similar variation also found by Ali and Tariq *et al.*¹⁴ for the binary system of benzyl alcohol with benzene.

Due to intermolecular interactions, structure of the molecules is changed, which affect the compressibility and thus a change in ultrasonic velocity. The ultrasonic velocity in a mixture is mainly influenced by the free length between the surfaces of the molecules of the mixtures. The inverse dependence of intermolecular free

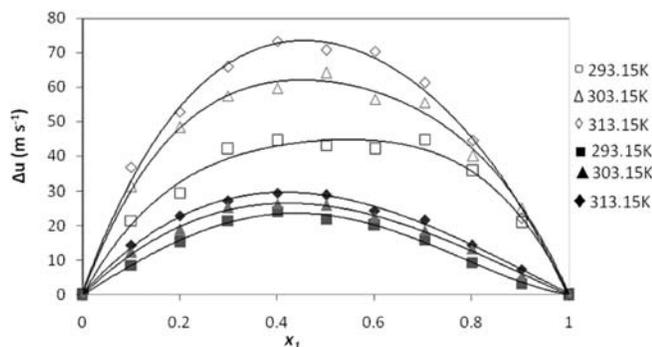


Fig. 4 Deviation in ultrasonic velocity (Δu) for the system (\square , \triangle , \diamond) PEGBE 206 + MAE and (\blacksquare , \blacktriangle , \blacklozenge) PEGBE 206 + 1-Butanol at 293.15, 303.15 and 313.15 K with respect to the mole fraction of PEGBE 206.

length and ultrasonic have been evolved from the model of sound propagation proposed by Eyring and Kincaid¹⁵. Our results for excess intermolecular free length and deviation in ultrasonic velocity support each other.

The role of internal pressure (π_i^E) in solution thermodynamics was recognized many years ago by Hilderband following earlier work of Prausnitz¹⁶. The variation of internal pressure may give some suitable information regarding the nature and strength of the forces existing between the molecules. In fact, the internal pressure is a broader concept and it is a measure of the totality of forces of the dispersion, ionic and dipolar interaction that contribute to be overall cohesion of the liquid systems¹⁷. For both the mixtures, values are found to be positive, and increases with a rise in temperature which indicates the presence of strong hydrogen bonding due to the charge transfer complex (Fig. 5). Similar results were observed by Parveen *et al.*¹⁸ in the mixtures of THF + o-cresol.

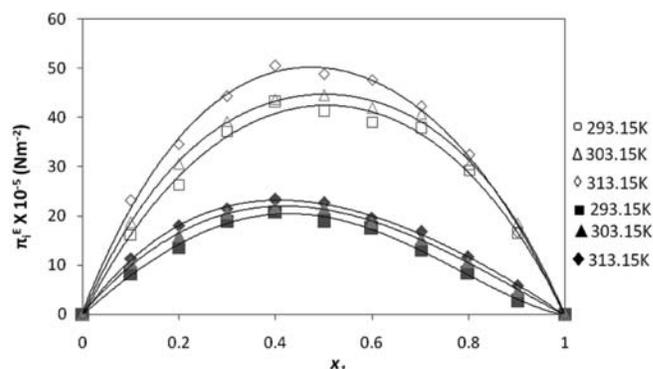


Fig. 5 Excess internal pressure (π_i^E) for the system (\blacksquare , \blacktriangle , \blacklozenge) PEGBE 206 + MAE and (\square , \triangle , \diamond) PEGBE 206 + 1-Butanol at 293.15, 303.15 and 313.15 K with respect to the mole fraction of PEGBE 206.

Since refractive index is closely related to the orientation, ordering and strength of constituent atomic oscillators of a given medium, it is expected that the variation of refractive index of the mixture with temperature and concentration of the solution can give valuable insight to the molecular rearrangement due to mixing. A close perusal of Fig. 6 shows that the ΔR_m values are negative for both the systems under investigation. The observed large negative values for both the systems indicate the presence of strong intermolecular bonding between PEGBE 206 and MAE/1-Butanol molecules. The effect of temperature on ΔR_m is not prominent in both the mixtures. Similar results

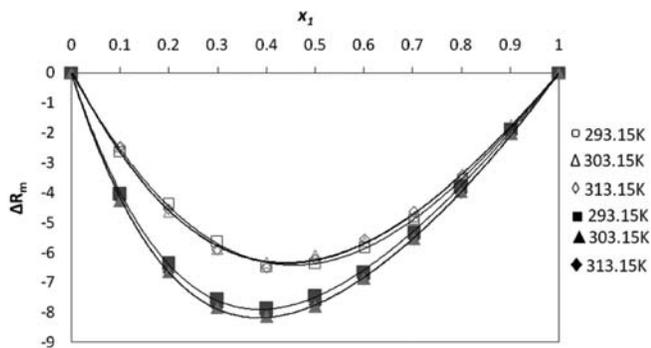


Fig. 6 Molar refraction deviation (ΔR_m) for the system (■, ▲, ◆) PEGBE 206 + MAE and (□, △, ◇) PEGBE 206 + 1-Butanol at 293.15 K, 303.15 K and 313.15 K with respect to the mole fraction of PEGBE 206.

have also been found by M. Yasmin for system PEG+ethanolamine, PEG+m-cresol and PEG+aniline¹⁹.

Redlich-Kister Polynomial Equation

The composition dependence of the excess properties is correlated by the Redlich-Kister polynomial equation. The values of excess parameters for each mixture were fitted to the Redlich-Kister polynomial equation²⁰ of the type,

$$Y^E = x_1(1-x_1) \sum_{i=1}^5 a_i (2x_1 - 1)^{i-1} \quad (7)$$

where a_i is the polynomial co-efficients.

$$\sigma(Y^E) \quad (8)$$

The values of the co-efficients a_i were obtained by the least squares method with all points weighted equally. In each case, the optimum number of co-efficients was ascertained from an examination of the variation of the standard deviation $\sigma(Y^E)$ with no. of co-efficients (p).

$$\sigma(Y^E) = \left[\frac{\sum (Y_{\text{expt}} - Y_{\text{cal}})^2}{n - p} \right]^{1/2} \quad (8)$$

where n is the number of measurements, p is the no. of parameters, Y_{expt} and Y_{cal} are the experimental and calculated parameters respectively. The values of co-efficient a_i evaluated using the method of least squares for the mixtures are given in Table 4 along with the standard deviations $\sigma(Y^E)$.

Conclusions

The density (ρ), speed of sound (u) and refractive index (n) of binary mixtures PEGBE 206 with MAE and 1- Butanol were measured at different temperatures. From the experimental data, various parameters, α , V_f , R_m , Δu , V_m^E and ΔR_m over the whole composite range were calculated. The values Δu^E and ΔR_m were fitted to Redlich Kister polynomial equation and standard deviations were calculated. Results indicate that there is a specific intermolecular interaction among the components of binary mixtures leading the possible hydrogen bonding formation between unlike molecule, 1-Butanol shows greater extent of interaction with PEGBE 206 than MAE.

Table 4 – Coefficients a_i of Redlich - Kister equation using the method of least squares for the mixtures along with the standard deviations.

Parameters	Temp(K)	a_1	a_2	a_3	a_4	a_5	$\sigma(Y^E)$
PEGBE 206 + 1- Butanol							
Δu (m s ⁻¹)	293.15	114.523	26.1741	70.0391	2.8648	-122.877	0.4012
	303.15	161.179	63.0599	72.9529	108.33	-61.2044	1.2832
	313.15	119.19	71.6761	63.7197	175.007	149.808	0.4656
ΔR_m	293.15	-413.505	-348.21	-240.75	-55.7239	41.6874	0.1903
	303.15	-403.197	-320.64	-298.32	-409.1	-270.102	1.7692
	313.15	-405.243	-299.75	-283.84	-460.474	-331.405	2.1535
PEGBE 206 + MAE							
γu (m s ⁻¹)	293.15	-130.2926	-130.0748	-121.9684	-86.2638	-21.2049	0.3328
	303.15	-145.0741	73.0193	-684.9443	-415.2566	856.6399	0.7159
	313.15	-125.6986	-129.0778	-188.8272	-178.5554	-85.584	0.8437
ΔR_m	293.15	-422.4018	-329.3091	-321.4609	-447.6781	-257.3066	0.3247
	303.15	-425.203	-329.2957	-321.9254	-443.2822	-262.9791	0.3801
	313.15	-417.5818	-343.2357	-424.7094	-654.6919	-412.2322	0.6418

References

- 1 **Kamila S.** and **Dash J.K.**, Studies on molecular interactions in different solvent extractants with n- butanol at temperatures 303.15K: A thermoacoustic investigation, *Journal of Molecular Liquids*, **172** (2012) 71-75.
- 2 **Arulaguppi M.** and **Baragi J.G.**, Physico chemical and excess properties of the binary mixtures of methyl cyclohexane + ethanol propane-1-ol + propane-2-ol + butan-1-ol at T (293.15, 303.15K and 308.15)K, *Chem Thermodynamics*, **38** (2006) 434-442.
- 3 **Bai E.M., Subha M., Swamy G.N.** and **Chowdoji K.R.**, Acoustical studies of molecular interactions in binary liquid mixtures of butoxy ethanol with some amines at 308.15K, *Ind. J. Pure Appl. Ultrason.*, **26** (2004) 79-83.
- 4 **Hammker R., Clegg R., Paderson P., Ridder P.** and **Rock S.**, Hydrogen bonded dimers and 2.86-m.u bond in alcohols, *J. Physics Chem.*, **72** (1968) 1837-1839.
- 5 **Lin W.** and **Tasy S.J.**, Nuclear magnetic resonance studies on the molecular association in some binary mixtures 1. Chloroform proton acceptor, *J. Phys. Chem.*, **74** (1970) 1037-1047.
- 6 **Pimental G.C.** and **Maclellan A.L.**, The Hydrogen bond *San Francisco, W.H. Freeman Co.* (1960) 29.
- 7 **Dixon W.D., Tucker E.** and **Becker E.**, Nuclear magnetic resonance study of solvent effect on hydrogen bonding in methanol, *J. Physics Chem.*, **74** (1970) 1396-1410.
- 8 **Ilokhani H.** and **Khanlarzadeh K.**, Densities, viscosities and refractive indices for binary and ternary mixtures of N-N dimethylacetamide (1) + n-methylbutan-2-ol (2) + Ethylacetate (3) at 298.15K for the liquid region and at ambient pressure, *J. Chem. Eng. Data*, **51** (2006) 1226-1231 .
- 9 **Resa J.M., Gonzalez C., De Landaluce S.O.** and **Lanz J.**, Densities, excess molar volume and refractive indices of ethylacetate and aromatic hydrogen binary mixtures. *J. Chem. Eng. Data*, **24** (2002) 995-1004.
- 10 **Singh S., Parveen S., Shukla D., Gupta M.** and **Shukla J.P.**, Volumetric, optical, acoustical and viscometric study of molecular association in binary mixtures of butylamine with 1-butanol and tert butanol, *Acta Phys. Pol. A* **111** (2007) 847-858.
- 11 **Aminbhavi T.M., Aralaguppi M.I., Horogappad S.B.** and **Balundgi R.H.**, Densities, viscosities, refractive indices and speed of sound for methylacetate = aliphatic alcohols (C1- C8), *J. Chem. Eng. Data* **38** (1993) 31-39.
- 12 **Bebek K.** and **Strugala-Wilczek A.**, Acoustical and thermophysical properties of binary mixtures of primary butanols with hexane and cyclohexane at 293.15K, *Int. J. Thermophys.* **31** (2009) 8-15.
- 13 **Juelin L., Mundhwa M., Tontiwachwuthikul P.** and **Henni A.**, Volumetric properties, viscosities and refractive indices for aqueous 2- (Methylamino) ethanol solutions from (293.15 to 343.15K), *J. Chem. Eng. Data*, **52** (2007) 560-565.
- 14 **Ali A.** and **Tariq M.**, Thermodynamic and transport behavior of binary liquid mixtures of Benzyl Alcohol with Monocyclic aromatics, *J. Mol. Liqs.*, **128** (2006) 50-55.
- 15 **Kincaid J.F.** and **Eyring H.**, Free volumes and free angles ratios of molecules in liquids, *J. Phys. Chem.*, **41** (1937) 249-257.
- 16 **Prausnitz J.M.**, Molecular thermodynamics of fluid phase equilibria. 2nd edn, *Prentice Hall Engle Wood Cliffs*, (1969) 45.
- 17 **Thirumarans S.** and **Karthikeyan N.**, Thermoacoustical and excess thermodynamic studies of ternary liquid mixtures of substituted benzenes in aqueous mixed solvent system at 303.15, 308.15 and 313.15K, *Int. J. Chem. Res.*, **3** (2011) 83-98.
- 18 **Parveen S., Singh S., Shukla D., Singh K.P., Gupta M.** and **Shukla J.P.**, Ultrasonic and volumetric study of N- H bond complexes in binary mixtures, *Acta Phys. Pol. A* **116** (2009) 1011-1017.
- 19 **Yasmin M., Gupta M.** and **Shukla J.P.**, Experimental and computational study on viscosity and optical dielectric constant of solutions of poly (ethylene glycol) 200, *Journal of Molecular Liquids* **160** (2011) 22-29.
- 20 **Redlich O.** and **Kister A.T.**, Algebraic representation of thermodynamic and classification of solutions, *Ind. Eng. Chem.*, **40** (1984) 345-348.

Synthesis and ultrasonic characterization of CuO-PVA nanofluids

A. Mathana Gopal^{1,*}, A. Moses Ezhil Raj² and J. Poongodi¹

¹Department of Physics, Kamaraj College (Affiliated to MS University, Tirunelveli), Thoothukudi-628003, Tamilnadu

²Department of Physics, Scott Christian College, Nagercoli-629003, Tamilnadu

*E-mail: matgop04@gmail.com

The molecular properties like transmission of sound in nanofluids undergo changes in highly associated systems and dependent on the cohesive properties of liquids. In the present investigation an attempt is made to calculate the ultrasonic velocity and density of the prepared nanoparticles at different weight percentage with the base fluid Poly Vinyl Alcohol (PVA). Copper oxide (CuO) nanofluid was synthesized by transforming an unstable $\text{Cu}(\text{OH})_2$ precursor to CuO in PVA under an ultrasonication. The result shows that CuO-PVA nanofluid can be synthesized using this method. The obtained dried precursor was annealed at 300°C. The annealed sample and the dried precursor were sonicated with an aqueous solution of PVA having concentration 4wt%. For comparison, the synthesized nanoparticles are characterized by X-Ray powder Diffractometry (XRD), Fourier Transform InfraRed Spectroscopy (FTIR), Diffuse Reflectance Spectroscopy (DRS) and analyzed. After ultrasonication UV-Visible Spectroscopy (UV-Vis), Ultrasonic velocity, density and adiabatic compressibility were analyzed and the results were discussed. There is a good agreement between the data produced by ultrasonic spectroscopy and other measurements.

Keywords: Nanofluid, Ultrasonication, Ultrasonic velocity, Density, Adiabatic compressibility.

Introduction

Nanofluids have attracted greater interest in recent years because of their enhanced thermal conductivity in comparison to that of the base fluids. Therefore, nanofluids can be used as a better heat transfer fluid in the heat exchange systems^{1,2}. Nanofluids find their wide applications in fields like electronic applications, transportation, industrial cooling application, heating buildings and reducing pollution, nuclear system cooling, space and defense, energy storage, solar absorption, friction reduction, magnetic sealing, antibacterial activity, nanodrug delivery, vehicular brake fluids, nanofluids based microbial, fuel cell, nanofluids based optical filters and sensors³. The nanofluids can be synthesized by dispersing a very small amount of Nanoparticles having size in the range 10-100 nm in the base fluid like water, ethylene glycol, polyvinyl alcohol, polyvinyl pyrrolidone *etc.* Using the ultrasonication the dispersion of the NPs in the base fluid is made uniform⁴.

Different methods have been developed to prepare nanofluids, such as the dispersing method⁵⁻⁹, physical

vapor condensation,^{4,10} and one-step chemical method¹¹, *etc.* In case of the dispersing method, synthesized nanoparticles are dispersed in liquid under stirring or ultrasonic vibration. For example, Lee and Choi prepared CuO nanofluid by dispersing commercial CuO nanoparticles in water under ultrasonic vibration⁵. It is a two-step method, in which the preparation of the nanoparticles and the preparation of the nanofluid are separated. Therefore, the nanoparticles may agglomerate during the drying, storage, and transportation process, leading to difficulties in the following dispersion stage. Consequently, the stability and thermal conductivity of nanofluid are not ideal. In addition, the production cost is high. To reduce the agglomeration of the nanoparticles, Choi *et al.* developed a one-step physical vapor condensation method to prepare Cu/EG nanofluid,^{4,10} in which Cu vapor was directly condensed into nanoparticles by contacting with a flowing ethylene glycol. The prepared nanofluid showed high stability as well as high thermal conductivity. However, it is difficult to synthesize nanofluid in large scale by this method, and the cost is also high. Recently, we developed a one-

step chemical method to prepare Cu nanofluid by reducing CuSO_4 with a reducing agent in EG¹¹.

From the foregoing view in CuO nanofluids the thermal conductivities behavior of the prepared nanofluids gives a high thermal conductivity than other conventional fluids by changing the precursor and volume fraction. In the present study, CuO nanoparticles were prepared then annealed and ultrasonicated to get nanofluids by changing the weight percentage of the CuO nanoparticles. The structural, optical and physical properties were experimentally measured for both nanoparticles and nanofluids. In my present work to increase the thermo-physical properties to get more heat transfer than other base fluids also by increasing the physical properties like ultrasonic velocity and density is done by increasing the weight percentage of CuO nanoparticles.

Experimental

All the reagents used in the experiment were of analytical purity. 20 mL of an EG solution of CuSO_4 (0.2 M) was put into a beaker, 8 mL of an EG solution of NaOH (1 M) was slowly dropped into the above solution under magnetic stirring at room temperature, and then a green precipitate formed in the solution. After the mixture was stirred for another 30 min, the precipitate was filtered using centrifuge machine and washed with DI water and it was dried at 80°C in the electric oven, and then wet $\text{Cu}(\text{OH})_2$ precursor was obtained

In order to obtain CuO nanoparticles, the dried copper hydroxide sample 'C' was annealed at temperature 300°C for 2 hrs. Finally the annealed sample of CuO Nanoparticles was denoted as 'CA' and it was grinded to get it in powdered form. An aqueous solution of PVA having concentration of 4 wt% was prepared. CuO Nanoparticles-PVA nanofluids of various concentrations were obtained by dissolving CuO Nanoparticles in the PVA solution with the aid of ultrasonicator.

Next, the suspension was ultrasonically vibrated for about 30 min in an ultrasonicator. The color of the suspension turned CuO nano fluid was obtained. All the prepared nanofluids samples S1, S1A were kept in air tight bottles.

For comparison, the synthesized nanoparticles are characterized by X-Ray powder Diffractometry (XRD), Fourier Transform InfraRed Spectroscopy (FTIR), Diffuse Reflectance Spectroscopy (DRS) and analyzed.

After ultrasonication UV-Visible Spectroscopy (UV-Vis), Ultrasonic velocity, density and adiabatic compressibility were analyzed and the results were discussed. There is a good agreement between the data produced by ultrasonic spectroscopy and other measurements.

2.1 XRD and FTIR

The X-ray diffraction patterns of the powdered samples of CuO nanoparticles C and CA were recorded on a X-ray diffractometer (XRD) with $\text{Cu-K}\alpha$ (1.5406 Å). The average crystalline size (D) has been calculated from the XRD pattern by using scherrer formula:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where λ is the wavelength of X-ray, β is full width of half maximum (FWHM) and θ is Bragg's angle of radians. The results are presented in the Fig. 1.

FTIR spectra were recorded by using Perkin Elmer FTIR Spectrometer-Spectrum Two in solid phase using the KBr pellets FTIR Spectrometer-Spectrum Two was used to identify the ingredients of the reaction in Samples S1, S2, S1A, and S2A Pellets

2.2 UV-Visible, DRS

A Perkin Elmer FTIR Spectrometer-Spectrum Two was used to identify the ingredients of the reaction in samples. The light absorption properties were investigated using SHIMADZU UV-2700 UV-Visible diffuse reflectance spectroscopy with the wavelength range of 200-900 nm.

2.3 Ultrasonic Velocity Measurements

The Ultrasonic velocities for pure PVA and nanofluids of different weight percentage of the samples C, CA at 0.2 wt%, 0.4 wt%, 0.6 wt%, 0.8 wt% and 1.0 wt% were measured using single-crystal variable path ultrasonic interferometer operating at 2 MHz frequency. The densities of nanofluids were measured using specific gravity bottle of 10 ml capacity.

Results and Discussion

3.1 Crystal Structure and FTIR

The typical XRD pattern of the CuO nano particles(C) and it was annealed at 300°C (CA) is shown in Fig. 1-2. The peak positions of the sample exhibited the monoclinic structure of CuO which was confirmed from

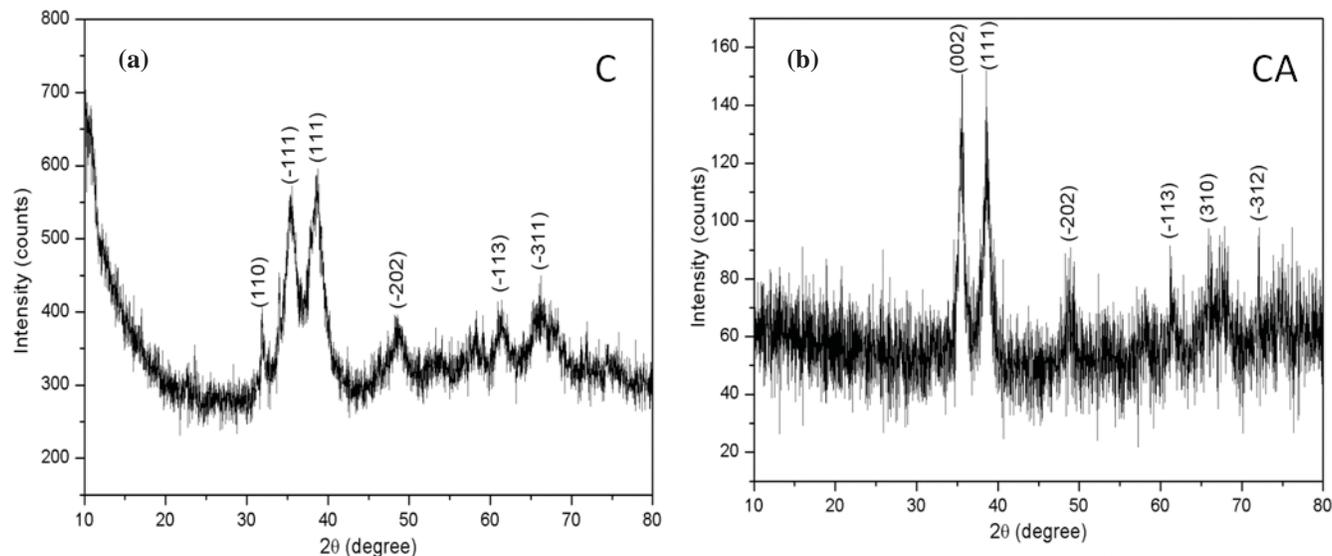


Fig. 1 XRD pattern for CuO Nanoparticles C and CA

the JCPDS card No 89-5899. Further, no other impurity peak was observed in the XRD pattern, showing the single phase sample formation. The crystalline size was calculated using the Scherrer formula, $D = 0.9 \lambda / \beta \cos \theta$, where λ is the wavelength of X-ray radiation, β is the full width at half maximum (FWHM) of the peaks at the diffracting angle θ . Crystallite size calculated by the Scherrer formula was found to be 13 nm. Lattice parameters and cell volumes were analyzed using UNIT CELL software. These values are in good agreement with the standard values reported by the JCPDS Card No 89-5899. In order to investigate the effect of temperature on CuO nanoparticles, samples were further annealed at 300°C. Figures 1 (a, b) exhibits the XRD spectra of CuO nanoparticles and it was annealed. It is clear from these Fig. 1 that the intensity of crystalline peaks increases with temperature, indicating an improvement in the samples crystallinity.

Simultaneously, the peaks become narrower as the temperature increases resulting in the increase of crystallite size. The variation of crystallite size and lattice parameters the results are presented in Table 1.

FTIR spectra (Fig. 2) were recorded in solid phase using the KBr pellets technique in the range of 4000-400 cm^{-1} with resolution of 1 cm^{-1} . FTIR spectra of CuO nanoparticles treated at 300°C is shown in Figure 2. The broad absorption peak around 2929 cm^{-1} to 3562 cm^{-1} is caused by OH stretching of absorbed water molecules. The peaks from 481 cm^{-1} to 1114 cm^{-1} indicates the Cu-O stretching and 1381 cm^{-1} to 1622 cm^{-1} indicates the Cu-O-H compounds. FTIR spectra exhibit only three vibrations: occurring at approximately 480 cm^{-1} , 530 cm^{-1} and 580 cm^{-1} for the sample, which can be attributed to the vibrations of CuO, confirming the formation of highly pure CuO nano particles¹².

Table 1 – Lattice parameter and crystalline size for samples C and CA

S. No.	Sample	Structure	Lattice parameter (Å)	Cell volume (Å ³)	Average crystalline size (nm)
1	C	Monoclinic	a =4.646 b = 3.487 c =5.131	81.834	13.359
2	CA	Monoclinic	a = 4.660 b = 3.457 c = 5.121	81.266	35.589

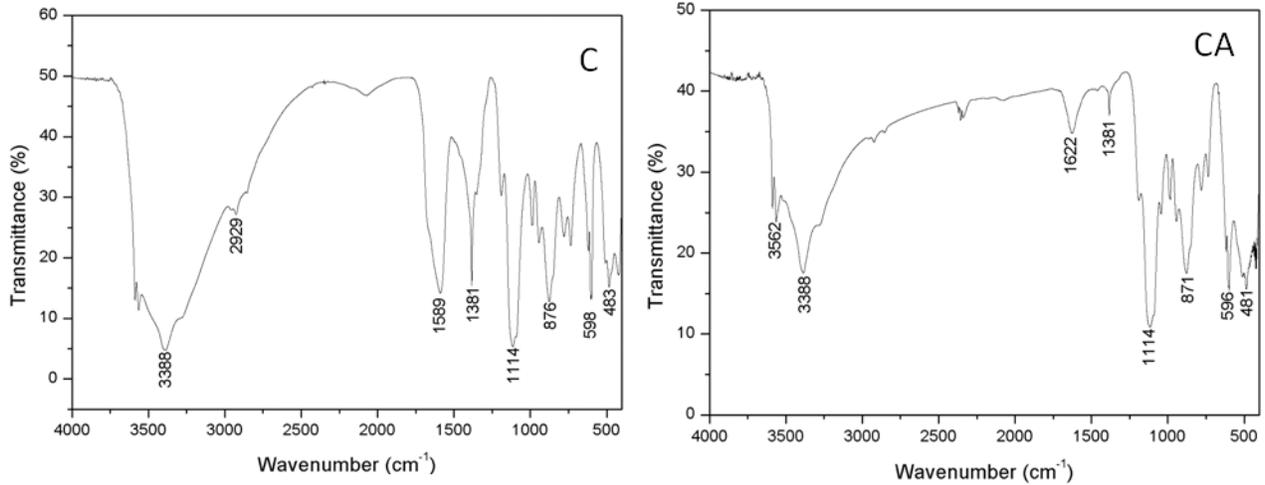


Fig. 2 FTIR spectra of CuO Nanoparticles C and CA

3.2 UV-Visible Spectra and DRS

UV-vis spectrum is recorded in the wavelength region 200-800 nm, using UV-vis spectrophotometer (UV2700). The spectrum is recorded for the samples C and CA of

copper oxides. Sample is prepared by 0.2 wt% (0.03g), 0.4 wt% (0.06g), 0.6 wt% (0.09g), 0.8 wt% (0.12g) and 1.0 wt% (0.15g) of samples C and CA was mixed with 15 ml of polyvinyl alcohol (PVA) solution and ultrasonicated it for 30 min. After setting the base line

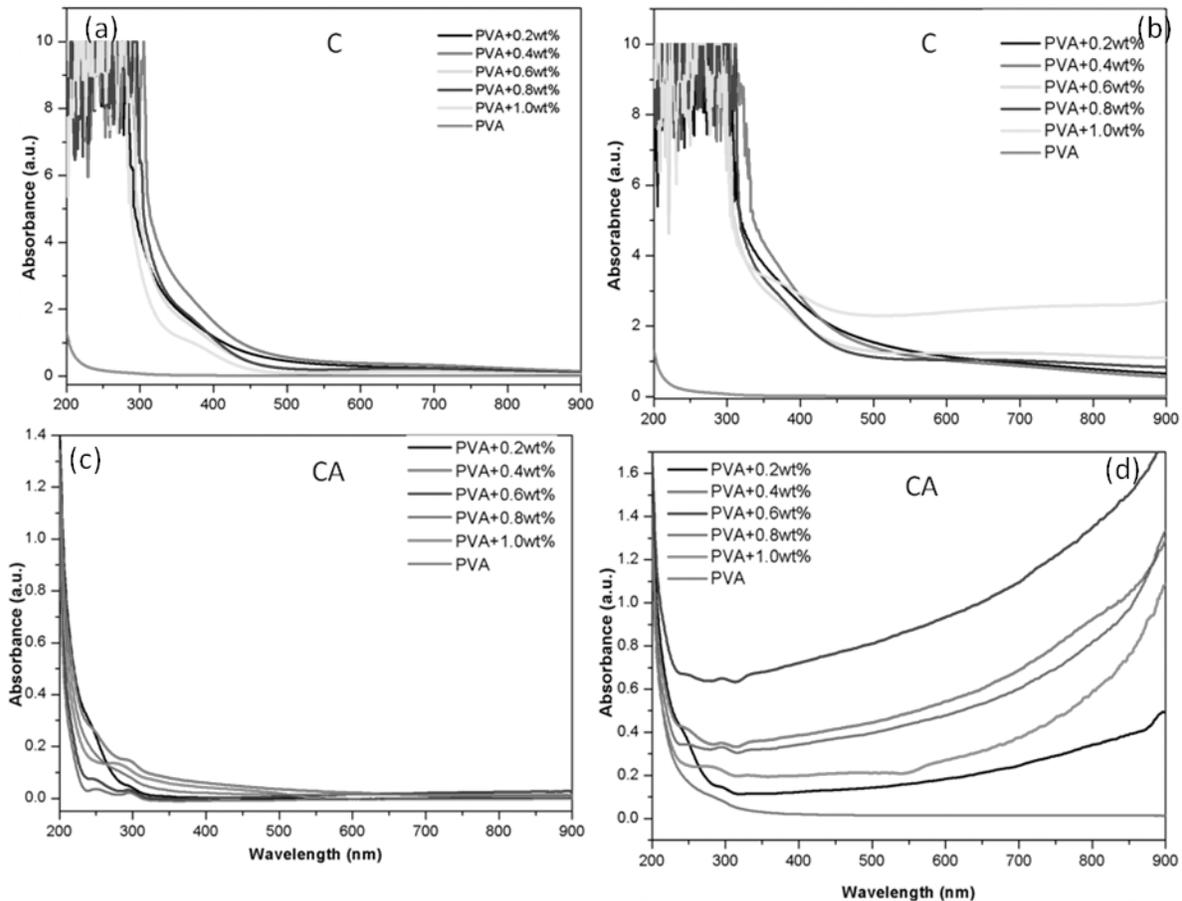


Fig. 3 UV-Visible spectra of the CuO-PVA nanofluid (a) Dilute C, (b) Mixed C, (c) Dilute CA, (d) Mixed CA

second compartment is replaced by the diluted nanofluid solution and the spectrum are analyzed.

Absorption spectra of pure PVA and CuO nanofluids C, CA was taken in the wavelength region of 200 - 800 nm shown in Fig. 3.

The absorption spectra taken for dilute nanofluid and mixed nanoparticles with fluids, for all the samples of C and CA. Here the small hump was observed in range of 250-300 nm for CA. For C it shows around 300-400 nm it absorbs the bulk CuO. By increasing the weight percentage of the sample the absorbance also get increases.

Diffuse reflectance spectra of CuO nanoparticles C and CA are shown in Fig. 4. Diffuse reflectance spectrum was recorded over the wavelength of 220 - 850 nm. Optical band gap of all the samples was calculated using Kubelka-Munk theory.

For p-type semiconductor, the direct band gap of the CuO nanoparticles was around 1.21-1.51 eV. The optical band gap for sample C and CA are 1.330(3) and 1.220(2)eV. From this we observed that in the sample C, the band gap decreases by annealing at 300°C the sample. For C band gap is 1.316 eV and after annealing CA it gets at 1.22eV¹³.

3.3 Ultrasonic velocity, Density and Adiabatic compressibility

Ultrasonic velocity gets increases with increasing the weight percentage of the samples C and CA this shows that the physical parameters of the sample changes by increasing the weight percentage. For CA, the velocity of the nanofluid is higher than C and also by increasing the weight percentage of sample CA the velocity get increases and it is shows in the Fig. 5. The cause behind this increase of ultrasonic velocity with increase in weight

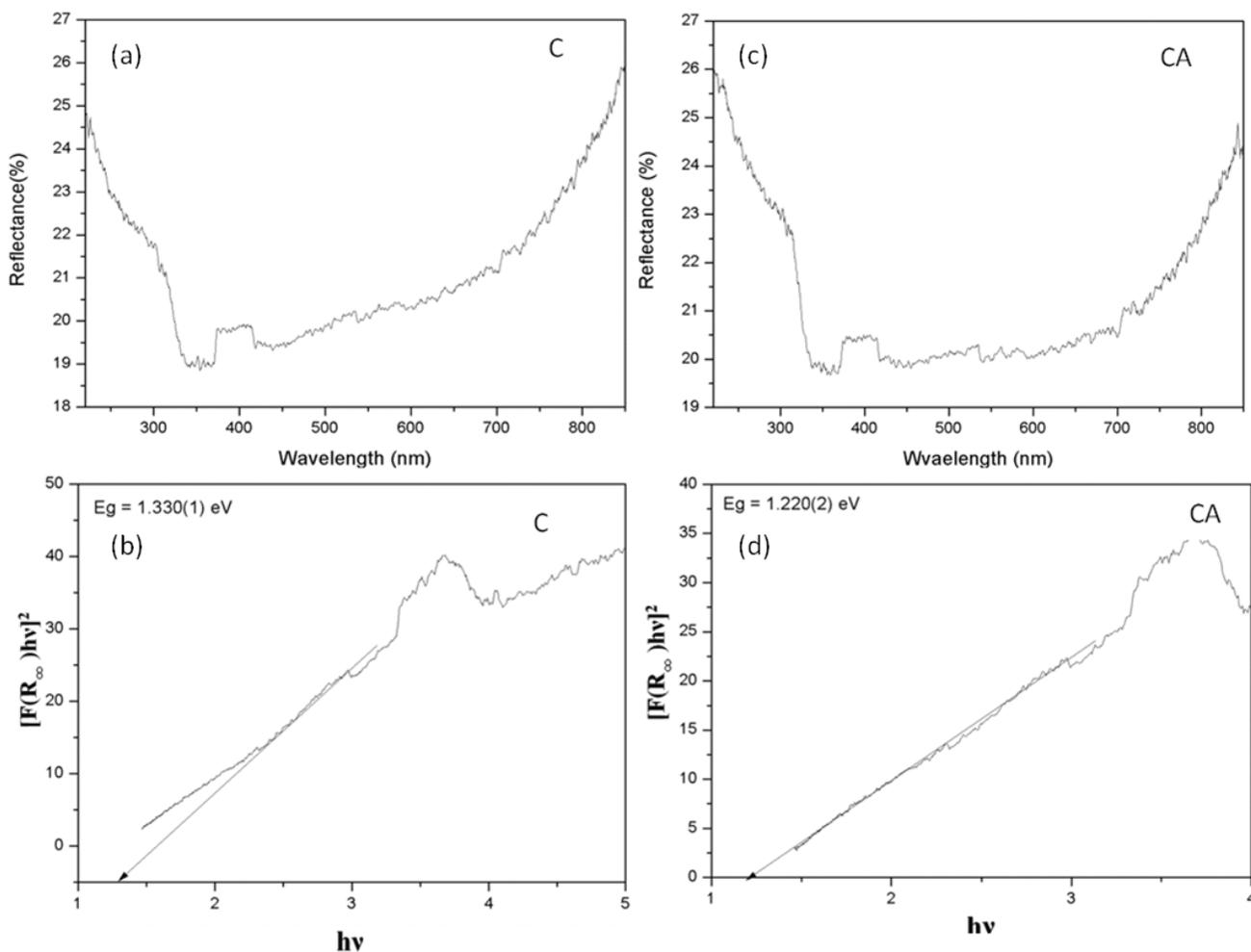


Fig. 4 DRS Spectra of CuO nanoparticles C & CA

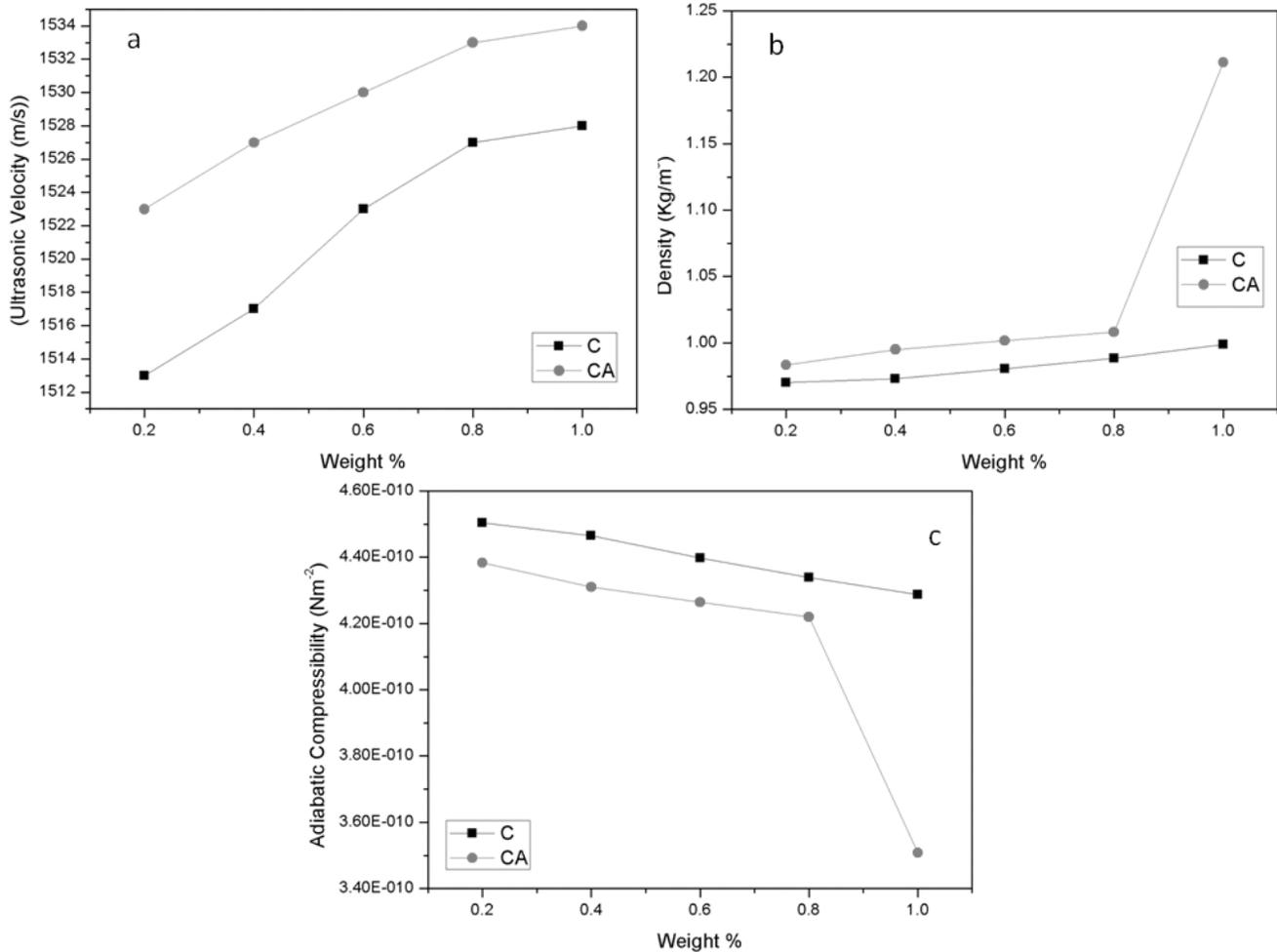


Fig. 5 Ultrasonic Velocity, Density and adiabatic compressibility of CuO-PVA nanofluids C & CA

percentage is due to weakening of interaction between nanosized particle and micro sized fluid molecule and also due to increase in density of nanofluid with increase of weight percentage. Ultrasonic velocity can be interpreted as the nanosized CuO particles have more surfaces to volume ratio and formation of hydrogen bonds with PVA molecules can absorb more PVA molecules on its surface, hence making the transport easy from one point to another point, which enhances the velocity.

Densities of the nanofluids are calculated by measuring the weight of the nanofluids using 10 ml of specific gravity bottle and also by using the standard value of density of water. The ultrasonic velocity and density of the water are also measured experimentally by the above procedure at room temperature velocity, $U = 1480$ m/s (Standard Value = 1480 m/s), Density, $\rho = 0.9978$ (kg/m³) (Standard value = 1 Kg/m³).

Here, the densities of the nanofluids also get increases

by increasing the weight percentage of the samples. Nanofluid CA has more density than C. Therefore, from this experiment, it is observed that the density of the fluid is get increases by annealing the CuO nanofluid. It is also observed from the plot that the ultrasonic velocity in CuO-PVA nanofluid increases slightly with concentration in the measured range (0.2 wt%, 0.4 wt%, 0.6 wt%, 0.8 wt% and 1.0 wt%) indicating that the nanofluids with small amount of NPs are less compressible¹⁴. According to Newton-Laplace's relation for adiabatic compressibility :

$$\beta = \frac{1}{\rho U^2} \text{Nm}^{-2} \quad (2)$$

where ρ is density of nanofluid and U is ultrasonic velocity in nanofluid. The cause behind this increase of ultrasonic velocity with increase in concentration is due to weakening of interaction between nanosized particle and micro sized fluid molecule and also due to increase

in density of nanofluid with increase of concentration¹⁵. It is shown in the Fig. 5.

Conclusion

In this present work, CuO - PVA nanofluids of different weight percentage (0.2 wt%, 0.4 wt%, 0.6 wt%, 0.8 wt% and 1.0 wt %) were prepared by one-step chemical method. The structural, optical and ultrasonic properties of the nanoparticles and nanofluids are characterized by using XRD, FTIR, DRS, UV-visible, ultrasonic velocity and density studies.

The XRD pattern reveals that the copper oxide is obtained and annealed at 300°C for 2 hrs. The samples (C, CA) are in monoclinic crystal structure. The average crystallite size of CuO nanoparticles is 10-40 nm, crystallite size of CuO NPs is increasing with increase of annealing temperature. Crystallite size of the sample C is greater than the annealed sample CA. FTIR confirms that the CuO metal ions are present around 481-1114 cm⁻¹. UV-visible shows that the absorbance peak of CuO nanoparticles around 250-300 nm. DRS also confirms that the direct band gap of the CuO nanoparticles around 1.21-1.51 eV.

This cell volume is a main role in ultrasonic velocity and density measurements. The velocity and density also get increases by increasing weight percentage but in the sample CA, this shows that the velocity get enhances than the nano fluid C. These nanofluid samples can be used successfully for any heat transfer management systems in industrial applications.

Acknowledgements

The authors sincerely acknowledged Dr. D. Pathinettam Padiyan, for his patient guidance valuable suggestions and the Thin Film Laboratory in M.S. University, Tirunelveli for the permission granted to do this experimental work.

References

- 1 **Choi S.U.S.**, Enhancing thermal conductivity of fluids with nanoparticles, *International Mechanical Engineering Congress and exhibition, San Francisco.*, **1** (1995) 99-105.
- 2 **Mishra G., Verma S.K., Singh D., Yadawa P.K. and Yadav R.R.**, Synthesis and ultrasonic characterization of Cu/PVP nanoparticles-polymer suspensions, *J. Acoustics*, **1** (2011) 9-14.
- 3 **Yu W. and Xie H.**, A review of nanofluids: preparation, stability mechanisms and applications, *J. Nanomaterials*, **2012** (2011) 1-17.
- 4 **Eastman J.A., Choi S.U.S., Li S., Yu W. and Thompson L.**, Anomalous increased effective thermal conductivities of ethylene glycol-based nanofluids containing copper nanoparticles, *J. Appl. Phys. Lett.*, **78** (2001) 718-723.
- 5 **Lee S., Choi S.U.S., Li S. and Eastman J.A.**, Measuring thermal conductivity of fluids containing oxide nanoparticles, *J. Heat Transfer*, **121** (1999) 280-289.
- 6 **Liu M.S., Lin M.C.C., Huang I.T. and Wang C.C.**, Enhancement of thermal conductivity with CuO for nanofluids, *Chem. Eng. Technol.*, **29** (2006) 72-77.
- 7 **Wen D. and Ding Y.**, Effective thermal conductivity of aqueous suspensions of carbon nanotubes (carbon nanotube nanofluids), *J. Thermophys. Heat Transfer*, **18** (2004) 481-485.
- 8 **Kulkarni D.P., Das D.K. and Chukwu G.A.**, Temperature dependent rheological property of copper oxide nanoparticles suspensions, *J. Nanosci. Nanotechnol.*, **6** (2006) 1150-1154.
- 9 **Wang B.X., Zhou L.P. and Peng X.F.**, Mechanism of heat transfer in nanofluids, *Prog. Nat. Sci.*, **14** (2004) 36-41.
- 10 **Choi S.U.S. and Eastman J.A.** Enhancing thermal conductivity of fluids with nanoparticles, Report No. ANL/MSD/CP-84938, CONF-951135-29 ON : DE 96004174; International Mechanical Engineering Congress & Exhibition San Francisco, CA (USA) 12-17 Nov. 1995. https://ecotert.com/pdf/196525-From_unit=edn.pdf; Accessed on 30/05/2018.
- 11 **Zhu H.T., Lin Y.S. and Yin Y.S.**, A novel one-step method for preparation for copper nanofluids, *J. Colloid Interface Sci.*, **277** (2004) 100-103.
- 12 **Zhengping Qiao., Yi Xie., Yingjie Zhu. and Yitan Qian.**, Synthesis of PbS/polyacrylonitrile nanocomposites at room temperature by Y-radiation, *J. Mater. Chem.*, **9** (1999) 1001-1002.
- 13 **Zabihi O. and Ghasemlou S.**, Nano-CuO epoxy composites: thermal characterization and thermal oxidative degradation, *Int. J. Poly. Analy. Char.*, **17** (2012) 108-121.
- 14 **Pandey V., Mishra G., Verma S.K., Wan M. and Yadav R.R.**, Synthesis and Ultrasonic investigations of CuO-PVA nanofluid, *J. Mater Sci. Appl.*, **3** (2012) 664-668.
- 15 **Mathana Gopal A. and Poongodi J.**, Study of thermodynamic properties in binary liquid mixtures through ultrasonic measurement, *J. Pure Appl. Ultrason.*, **39**(2016) 122-126.

Studies of ultrasonic and acoustic parameters of Cu (II) surfactant of fresh and treated sesame and soyabean oils at high temperature for different time

Renu Bhutra¹, Rashmi Sharma² and Arun Kumar Sharma^{3,*}

Department of Chemistry

¹Rajesh Pilot Government Polytechnic College Dausa-303303, India

²S.P.C. Government College Ajmer-305001, India

³Government P.G. College, Jhalawar-326001, India

*E-mail: sharmaarun423@gmail.com

Colloid chemical behavior and micellar characteristics of Cu (II) soaps derived from sesame and soyabean oils, (fresh oils and treated for 15 and 60 min.) at high temperature in benzene have been investigated and verified by ultrasonic velocity measurement. From these values, the specific acoustic impedance Z , adiabatic compressibility β_{ad} , intermolecular free length L_f , apparent molar compressibility ϕ_k , molar sound velocity R , primary solvation number S_n have been calculated. The results have been analyzed in terms of Masson's equation. The results have been explained on the basis of solute-solvent interactions. The decrease in β and L_f with increasing concentration of the complex is indicating that there is sufficient solute-solvent interaction due to which micellar alignment is considerably affected.

Keywords: Copper surfactants, benzene, sesame oil, soyabean oil, ultrasonic, solute-solvent interaction.

Introduction

Ultrasonic wave in recent years, acquired the status of an important probe for the study of structure and properties of matter in basic essence. Many workers found the ultrasonic propagation parameters, determined Intermolecular free-Length (L_f) in liquids and liquid mixtures using the Jacobson's relation, studied many acoustical parameters of liquid fluorine and H₂S, CO, CD and HCN, C₂N₂ and POCl₃ and also plastic crystals parameters like adiabatic compressibility β_{ad} etc. of solvent, solvent mixtures and the soap solutions have also been made¹⁻². Ultrasonic parameters of solvent and solvent mixtures have also been studied at various temperatures³⁻⁴. Properties of surface active solutions are very important to access the thermodynamic, acoustic and transport aspects⁵. Ultrasonic technique is a powerful means for characterizing the various aspects of physicochemical behavior of the system and also for studying the interaction between the molecules⁶. A number of workers⁷⁻⁸ have discussed the physico-chemical aspects of ultrasonic velocity and related parameters on different types of soaps and detergents.

The Gruneisen parameter and internal pressure obtained from ultrasonic velocity and density data play a significant role in understanding internal structure, clustering phenomenon and quasi-crystalline nature of binary mixture⁹. Ultrasonic measurements have also been used to determine solvation number in aqueous media¹⁰. The present work deals with the determination of ultrasonic velocity measurements which have been used to obtain information regarding various acoustic parameters and solute-solute interactions of Cu (II) surfactants of sesame and soyabean oils (fresh oils and treated with 15 and 60 min.) at high temperature in non-aqueous solvent benzene at 303.15 K to access the effect of solvent molecules on the micellar nature of solute molecule.

Experimental

All the chemicals used were of LR/AR grade. Six copper soap was prepared by refluxing two edible oils *i.e.* untreated and treated sesame (extracted from kernels and purified) and soyabean (direct from market) at 180°C for 15 minutes and 60 minutes with ethyl alcohol and 2N KOH solutions for 3-4 hrs (Direct Metathesis)¹¹.

The copper soaps are abbreviated as follows :

1. Copper - sesame soap (CSe)
2. Copper - soyabean soap (CSo)
3. Copper - sesame soap treated for 15 min at high temperature. (CSe₁₅)
4. Copper - soyabean soap treated for 15 min at high temperature. (CSo₁₅)
5. Copper - sesame soap treated for 60 min at high temperature. (CSe₆₀)
6. Copper - soyabean soap treated for 60 min at high temperature. (CSo₆₀)

The underlying principle of ultrasonic experimental technique used in the measurement of velocity (U) is based on the accurate determination of the wavelength (λ) of the medium. Ultrasonic waves of known frequency (f) are produce by a quartz plate fixed at the bottom of the cell. Ultrasonic interferometer with accuracy of $\pm 0.03\%$ was used for the measurements of ultrasonic velocities in various solutions at a fixed frequency 2 MHz. The total distance d (1 cm) thus moved by the micrometer gives the value of wavelength with the help of the following relation¹².

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

Once the wavelength is known, the ultrasonic velocity U in the solution can be calculated with the help of the following relation:

$$U = \lambda \times f \quad (2)$$

Measurement of Density:

Ostwald's modification of Sprengel' spyknometer with a volume of about 10 ml was used for measuring the density of the soap solution in the thermo stated bath at 298.15 K. The density of the solutions was calculated by the following relationship:

$$\rho = w/w_0 \quad (3)$$

Where w and w_0 are the weights (same volume) of solution and water respectively.

Results and Discussion

Acoustic parameters

The specific acoustic impedance Z , adiabatic compressibility β , intermolecular free length L_f , apparent molar compressibility ϕ_k , molar sound velocity

R and primary solvation number S_n have been calculated by using the following relationships¹³.

$$Z = U \rho \quad (4)$$

$$\beta = \frac{1}{U^2 \rho} \quad (5)$$

$$L_f = K \sqrt{\beta} \quad (6)$$

$$\phi_k = \left[1000 \cdot \frac{\beta \rho_0 - \beta_0 \rho}{c \rho_0} \right] + \frac{\beta M}{\rho_0} \quad (7)$$

$$R = M \cdot (U)^{1/3} \rho_0 \quad (8)$$

$$M = X_1 M_1 + X_2 M_2 \quad (9)$$

$$S_n = \left[\frac{n^0}{n} \right] \cdot \left[1 - \frac{v \beta}{n^0 v^0 \beta^0} \right] \quad (10)$$

Where β_0 , β , d_0 , d , n_0 , n , \bar{V}_0 and \bar{V} are *adiabatic compressibility, density, number of moles and molar volume of solvent and complex (solute) solution respectively*. K (6.31×10^4), c and U respectively are the temperature dependent Jacobson's constant, concentration of the solution and ultrasonic velocity. The expression for molar volume of the solvent \bar{V}_0 and soap solution \bar{V} may be written as¹⁴.

$$\bar{V} = X_1 M_1 + X_2 M_2 \quad (11)$$

$$\bar{V}_0 = X_1 M_1 + X_2 M_2 \quad (12)$$

In Eqs. (11) and (12), M represents the molecular weight and X the mole fraction of the component. Here the subscript 1 and 2 refer to solute and solvent respectively. The data clearly indicate that the values of u , Z , ϕ_k , S_n and R increase whereas the values of β_{ad} and L_f decrease consistently with increase in the soap concentration. The increase in ultrasonic velocity may be attributed to the solute-solvent interaction. The increase in the values of specific acoustic impedance Z with soap concentration c can be explained on the basis of lyophobic interaction between soap and solvent molecules, which increases the intermolecular distance leaving relatively wider gaps between the molecules and becoming the main cause of impedance in the propagation of ultrasound waves¹⁵. The decrease in intermolecular free length L_f with increase in soap

concentration indicates that there is significant interaction between soap and solvent molecules and that the structural arrangement is considerably affected. The decrease in adiabatic compressibility of the soap solutions with increasing soap concentration may be interpreted on the basis of the fact that the soap molecules are surrounded by a layer of solvent molecules firmly bounded. This results in the increase in the internal pressure and in lowering the compressibility of the solution *i.e.* solution becomes harder to compress. The above findings may be supported by the fact that as the concentration of solute increases, a larger portion of

solvent molecules are electrostricted and the amount of bulk solvent decreases causing the compressibility to decrease. In the present study, du/dc is negative which indicates the electrostriction of solvent molecule. The variation in the solvation number with concentration is in fairly good agreement with the results proposed by various workers for the solution of lanthanum nitrate in methanol and ethanol. The values of molar sound velocity R increase linearly with increase in soap concentration. The values of du/dc for Copper soaps are positive showing resemblance with the results of other workers.

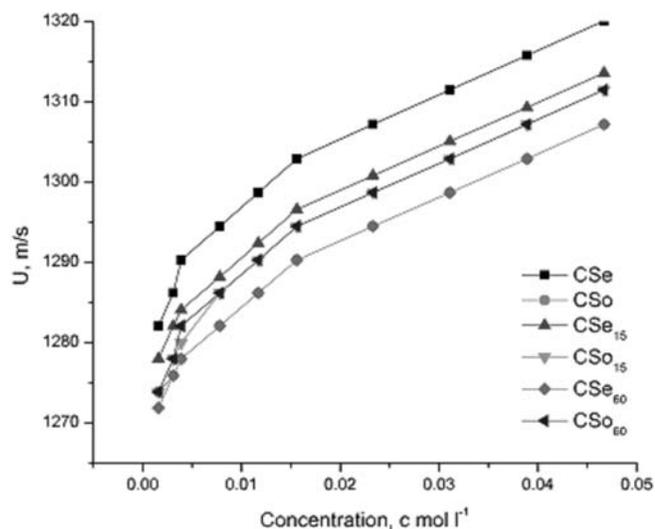


Fig. 1 Plots of u versus c for copper soaps derived from untreated and treated sesame and soyabean oils at high temperatures in benzene.

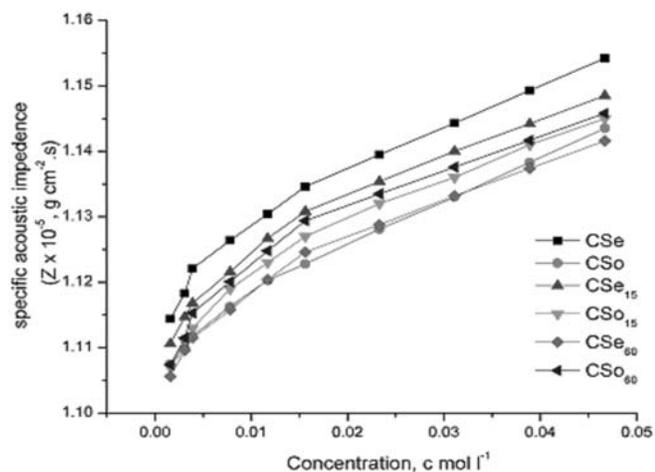


Fig. 2 Plots of z versus c for copper soaps derived from untreated and treated sesame and soyabean oils at high temperatures in benzene.

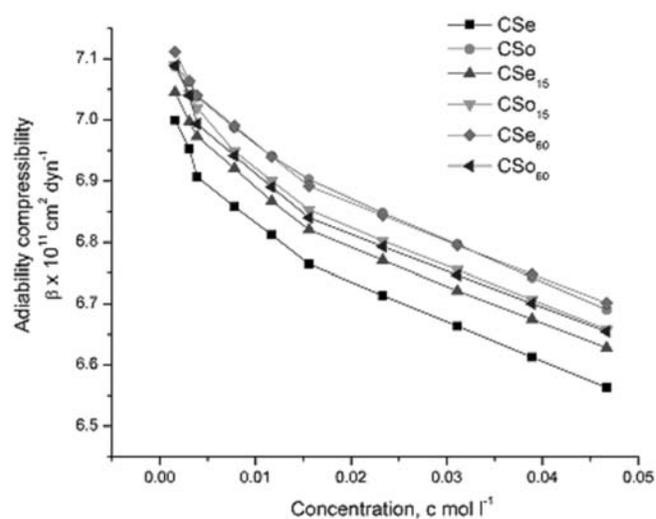


Fig. 3 Plots of β_{ad} versus c for copper soaps derived from untreated and treated sesame and soyabean oils at high temperatures in benzene.

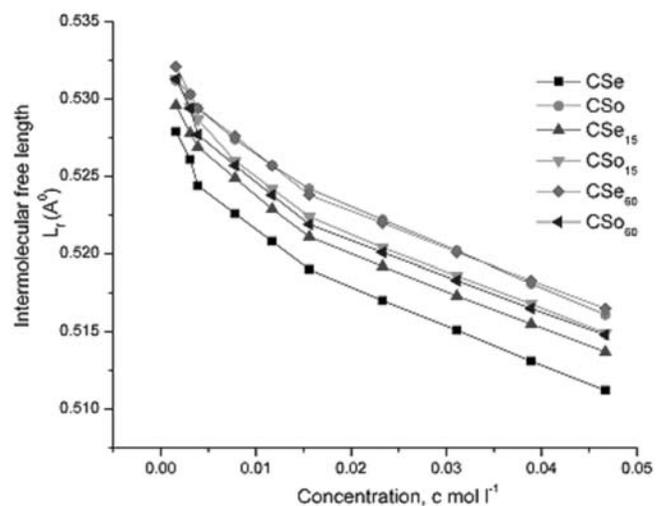


Fig. 4 Plots of L_f versus c for copper soaps derived from untreated and treated sesame and soyabean oils at high temperatures in benzene.

Micellar Features

The plots of u , Z , β_{ad} and L_f versus c show break at a definite soap concentration, which corresponds to the CMC of these soaps (Figs. 1-4).

At the CMC hydrocarbon chain structure of soap molecule allows extensive contact between adjacent chains possibly accompanied by change in vibrational and rotational degree of freedom of methylene group. The values of CMC observed for all the parameters of these soaps are recorded in Table 1. From the Table 1, it is clear that CMC follows the order:¹⁶

$$CSO > CSe, CSe_{15} < CSO_{15}, CSe_{60} > CSO_{60}$$

This order of CMC is same as observed by other physical properties.

The variation of the ultrasonic velocity with soap concentration c is expressed by the equation :

$$u = u^0 + Gc \quad (13)$$

Here u^0 is the ultrasonic velocity in the solvent. Here G is Gruneisen constant. The value of G is obtained from the slope of the linear plots of u versus c below CMC. The plots of ultrasonic velocity versus soap concentration are extrapolated to zero soap concentration. It is found that the extrapolated values of ultrasonic velocity is in agreement with the experimental value of the velocity in the solvent, indicating that the soap molecules do not aggregate to an appreciable extent below CMC¹⁷. It is interesting to point out that values of the parameters u , Z , β_{ad} and L_f with respect to copper soaps of different untreated oils follow the order:

$$\begin{aligned} [u] &\Rightarrow CSe > CSO [u] \Rightarrow CSe_{15} > CSO_{15} [u] \Rightarrow CSO_{60} > CSe_{60} \\ [Z] &\Rightarrow CSe > CSO [Z] \Rightarrow CSe_{15} > CSO_{15} [Z] \Rightarrow CSO_{60} > CSe_{60} \\ [\beta] &\Rightarrow CSe < CSO [\beta] \Rightarrow CSe_{15} < CSO_{15} [\beta] \Rightarrow CSO_{60} < CSe_{60} \\ [L_f] &\Rightarrow CSe < CSO [L_f] \Rightarrow CSe_{15} < CSO_{15} [L_f] \Rightarrow CSO_{60} < CSe_{60} \end{aligned}$$

From the comparison of all the results for Copper soaps of untreated and treated oils, the values of u and Z follow the order:¹⁸

$$CSe > CSe_{15} > CSe_{60} \quad CSO > CSO_{60} > CSO_{15}$$

As observed, the values of ϕ_k increase sharply up to the critical micelle concentration and after CMC it increases gradually. ϕ_k is a function of concentration and its value is found to be in good agreement with that obtained from the following Masson equation¹⁹.

$$\phi_k = \phi_{0k} + S_k \sqrt{c} \quad (14)$$

Where ϕ_k is the limiting apparent molar compressibility and S_k is a constant. The plots of apparent molar compressibility ϕ_k against square root of soap concentration \sqrt{c} are characterized by the intersection of two straight lines at the CMC (Fig. 5).

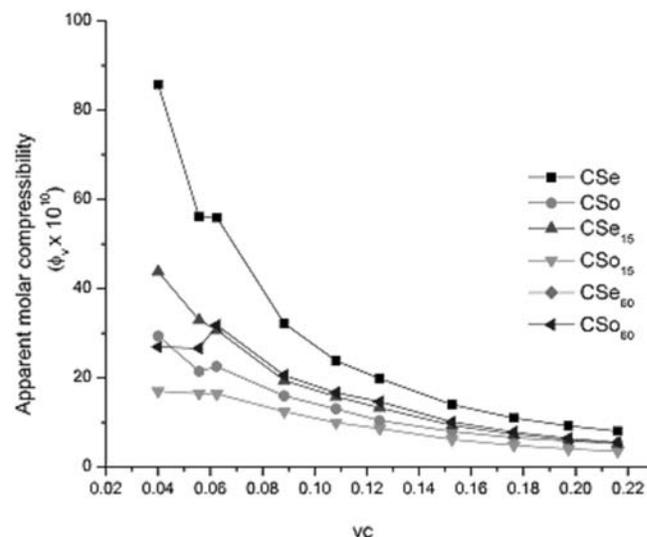


Fig. 5 Plots of S_k versus \sqrt{c} for copper soaps derived from untreated and treated Sesame and soyabean oils at high temperatures in benzene.

Table 1 – Values of CMC of copper soaps derived from untreated and treated oils.

Plot	Name of the soap					
	CSe	CSO	CSe ₁₅	CSO ₁₅	CSe ₆₀	CSO ₆₀
u versus c	0.012	0.0155	0.0145	0.0185	0.0230	0.0140
Z versus c	0.012	0.015	0.0145	0.0185	0.0230	0.0140
β_{ad} versus c	0.012	0.015	0.0145	0.0185	0.0230	0.0140
L_f versus c	0.012	0.015	0.0145	0.0185	0.0230	0.0140
ϕ_k versus \sqrt{c}	0.0117	0.0159	0.0148	0.019	0.0237	0.0144

Table 2 – Values of various constants obtained from Masson's equation for copper soaps derived from treated and non-treated oils in benzene.

Name of the soap	$u \text{ ms}^{-1}$	$G \times 10^{-5}$	$\phi_{k1}^0 \times 10^8$	$\phi_{k2}^0 \times 10^8$	$S_{k1} \times 10^8$	$S_{k2} \times 10^8$
CSe	1278.5	1.9209	-95.5	-28.0	2.9042	0.3639
CSO	1272.0	1.1503	-38.0	-14.0	0.9004	0.1763
CSe ₁₅	1276.0	1.2799	-51.5	-26.0	1.2130	0.3443
CSO ₁₅	1271.0	1.1503	-23.5	-17.5	0.3939	0.2493
CSe ₆₀	1269.5	0.7812	-15.0	-10.0	0.2308	0.1316
CSO ₆₀	1271.5	1.6318	-36.5	-27.0	0.7399	0.4040

Values of ϕ_k are evaluated from the intercepts of the linear plots of ϕ_k versus \sqrt{c} and values of S_k are calculated from the slope of these plots. In view of the two intersecting straight lines for ϕ_k versus \sqrt{c} plots, it is reasonable to determine two values of parameters ϕ_k and S_k below and above *CMC* designated as ϕ_k , S_{k1} and ϕ_k , S_{k2} respectively and recorded in Table 2.

From the Table 2, it is clear that the values of ϕ_{k1} and ϕ_{k2} are negative for all these copper soaps. The negative ϕ_k values may be due to the loss of compressibility of solvent due to strong electrostrictive forces in the vicinity of ions. The change in the values of ϕ_k and S_k below and above *CMC* suggests that there is a phenomenal change in the micellar agglomeration²⁰.

A perusal of the data shows the similar facts as observed for other Copper soaps under reference, *i.e.* the values of limiting apparent molar compressibility (ϕ_{k1} and ϕ_{k2}) are negative and are in the following order:

$$\phi_{k2} > \phi_{k1} \text{ and } S_{k1} > S_{k2}$$

It is apparent from that *CMC* values follow the order:

$$\text{CSO} > \text{CSe}, \text{CSe}_{15} < \text{CSO}_{15}, \text{CSe}_{60} > \text{CSO}_{60}$$

The results are in agreement with the fact that there is decrease in the *CMC* with the increase in average molecular weight of the soap. This order of *CMC* is same as observed by other physical properties.

Conclusion

The nonlinear variation of ultrasonic velocity and other acoustical parameters with molar concentration of copper surfactants derived from sesame and soyabean oil with non-polar pure benzene shows the intermolecular interaction occurs in constituent molecules. The decrease in adiabatic compressibility of the soap solutions with increasing soap concentration may be interpreted on the

basis of the fact that the soap molecules are surrounded by a layer of solvent molecules firmly bounded. This results in the increase in the internal pressure and in lowering the compressibility of the solution. This provides useful information about the nature of intermolecular forces existing in the mixture during their applications in various fields.

Acknowledgment

The authors pay their sincere gratitude to UGC, New Delhi for Finance and Principal, S.D. Government College, Beawar, Rajasthan (India) and S.P.C. Government College Ajmer for providing necessary research facilities to accomplish this study.

References

- 1 **Saxena M., Sharma R. and Sharma A.K.**, Micellar Features of Cu (II) surfactants derived from edible oils "ISBN 978-620-2-01906-4" LAP Lambert Academic Publishing Germany (2017).
- 2 **Sharma A.K., Saxena M. and Sharma R.**, Synthesis, spectroscopic and fungicidal studies of Cu (II) soaps derived from groundnut and sesame oils and their urea complexes, *Bulletin of Pure and Applied Sciences*, **36**(2) (2017) 26-37.
- 3 **Khan S., Sharma R. and Sharma A.K.**, Acoustic studies and other acoustic parameters of Cu(II) soap derived from nonedible neem oil (*azadirachta indica*), in non-aqueous media at 298.15, *Acta Acustica* **104** (2018) 277-283
- 4 **Sharma A.K., Saxena M. and Sharma R.**, Synthesis, spectroscopic and biocidal activities of environmentally safe Agrochemicals, *J. Biochem. Tech.* **7**(3) (2018) 1139-1147.
- 5 **Tank P., Sharma R. and Sharma A.K.**, Studies of Ultrasonic and acoustic parameters of complexes derived

- from Copper (II) surfactant of mustard oil with N and S atoms containing ligands in non- aqueous media (benzene) at 303.15 K. *J. Acous. Soc. Ind.* **44**(2) (2017) 87-99.
- 6 **Bhutra R., Sharma R. and Sharma, A.K.**, Viscometric and CMC studies of Cu(II) surfactants derived from untreated and treated groundnut and mustard oils in non-aqueous solvent at 298.15 K, *J. Inst. Chemists.* **90** (2017) 29-47.
 - 7 **Sharma S., Sharma R. and Sharma A.K.**, Synthesis, Characterization, and thermal degradation of Cu (II) Surfactants for sustainable green chem, *Asian J. Green Chem.* **2**(2) (2017) 129-140.
 - 8 **Sharma S., Sharma R., Heda L.C. and Sharma, A.K.**, Kinetic parameters and photo degradation studies of copper soap derived from soybean oil using ZnO as a Photo catalyst in solid and solution Phase, *J. Inst. Chemists.* **89**(4) (2017) 119-136.
 - 9 **Tank P., Sharma R. and Sharma A.K.**, A pharmaceutical approach and antifungal activities of copper Soaps with their N and S donor complexes derived from mustard and soyabean oils, *Glob. J. Pharmaceu. Sci.* **3**(4) (2017) GJPPS.MS.ID.555619.
 - 10 **Khan S., Sharma R. and Sharma A.K.**, Ultrasonic studies of Cu (II) Soap derived from seed oil of Pongamia pinnata (Karanj), in non-aqueous binary and ternary systems at 298.15K. *Malaysian J. Chem.* **19**(2) (2017) 99-110.
 - 11 **Sharma A.K., Saxena M. and Sharma R.**, Ultrasonic studies of copper soaps urea complexes derived from mustard and soyabean oils. *J. Phy. Sci.* (2018) (Accepted).
 - 12 **Sharma A.K., Saxena M. and Sharma R.**, Ultrasonic studies of Cu (II) soaps derived from mustard and soybean oils. *J. Pure Appl. Ultrason*, **39**(3) (2017) 92-99.
 - 13 **Tank P., Sharma R. and Sharma A.K.**, Micellar features and various interactions of copper soap complexes derived from edible mustard oil in benzene at 303.15 K. *Curr. Phy. Chem.* **8**(1) (2018) 46-57.
 - 14 **Sharma R. and Sharma A.K.**, Natural edible oils: comparative health aspects of sesame, coconut, mustard (rape seed) and groundnut (peanut) a biomedical approach, *Biomed. J. Sci. Tech. Res.* **1**(5) (2017) BJSTR.MS.ID.000441.
 - 15 **Tank P., Sharma A.K. and Sharma R.**, Thermal behaviour and kinetics of copper (II) soaps and complexes derived from mustard and soyabean oil, *J. Anal. Pharm. Res.* **4**(2) (2017) 1-5.
 - 16 **Sharma A.K., Saxena M. and Sharma R.**, Ultrasonic studies of Cu (II) Soaps derived from Groundnut and Sesame oils, *Tenside. Surf. Det.* **55**(2) (2018) 127-134.
 - 17 **Bhutra R., Sharma R. and Sharma A.K.**, Synthesis, Characterization and fungicidal activities of Cu (II) surfactants derived from groundnut and mustard oils treated at high temperatures, *J. Inst. Chemists.* **90**(3) (2018) 66-80.
 - 18 **Sharma A.K., Sharma R. and Saxena M.**, Biomedical and antifungal application of Cu(II) soaps and its urea complexes derived from various oils, *Open Access J. Trans. Med. Res.* **2**(2) (2018) 40-43.
 - 19 **Sharma A.K., Sharma S. and Sharma R.**, Thermal degradation of Cu (II) metallic soaps and their Characterizations. A pharmaceutical application, *Chro. Phar Sci.*, **1**(5) (2017) 312-319.
 - 20 **Sharma A.K., Saxena M. and Sharma R.**, Acoustic studies of copper Soap-urea complexes derived from groundnut and seasam oils. *J. Phy. Studies*, **21**(4) (2017) 4601-6.

Comparative study of molecular interactions in ternary liquid mixtures by ultrasonic techniques

Manoj Kumar Praharaj

Department of Physics, Ajay Binay Institute of Technology, Cuttack-753014, India
E-mail: m_praharaj@rediffmail.com

The ultrasonic velocity, density and viscosity have been measured for the ternary mixture of benzene, toluene and pyridine successively with N, N-dimethylformamide in cyclohexane at different temperatures and at frequency 2 MHz for different concentrations of component liquids. The experimental data of velocity, density and viscosity have been used for a comparative study of the molecular interaction in the different mixtures using different parameters such as adiabatic compressibility, free length, free volume and surface tension. Variation in the above parameters for the different mixtures is indicative of the nature of interaction between them.

Keywords: Ternary mixture, ultrasonic velocity, free length, surface tension.

Introduction

Now a day, ultrasonic studies are extensively used for characterizing the thermodynamic properties of liquid mixtures. This method plays an important role in understanding the nature of molecular interactions. A large number of studies have been made on the molecular interaction in liquid mixtures of different organic and inorganic liquid mixtures¹⁻⁵.

Velocity of sound waves in a medium is fundamentally related to the binding forces between the molecules. The variation of ultrasonic velocity and other thermodynamic parameters in ternary liquid mixtures with changing mole fraction of one or two components has been investigated by different authors⁶⁻¹⁰.

In the present paper, the molecular interaction between ternary liquid mixtures consisting of N, N-dimethyl formamide, cyclohexane along with benzene, toluene and pyridine was studied at different temperatures.

Mixture-I : N, N DMF + Cyclohexane + Benzene
Mixture-II : N, N DMF + Cyclohexane + Toluene
Mixture-III : N, N DMF + Cyclohexane + Pyridine

Molecules of Cyclohexane are non-polar, molecules of toluene is polar in nature due to presence of electron releasing methyl group, where as that of N, N-dimethylformamide (DMF) is highly polar.

Experimental

Ternary mixtures with different concentrations were prepared by taking analytical reagent grade and spectroscopic reagent grade chemicals with minimum assay of 99.9%. All the component liquids were purified by the standard methods¹¹. In all the mixtures, the mole fraction of the second component, cyclohexane ($X_2 = 0.4$), was kept fixed while the mole fractions of the remaining two (X_1 and X_3) were varied from 0.0 to 0.6, so as to have the mixture of different concentration. The density, viscosity, and ultrasonic velocity were measured as a function of concentration of the ternary liquid mixture at 288 K, 298 K and 308 K and at frequency of 2 MHz.

Ultrasonic velocity at different temperatures were measured by using an ultrasonic interferometer with the accuracy of $\pm 0.1 \text{ ms}^{-1}$. The densities of the mixtures were measured using a 10-ml specific gravity bottle by relative measurement method with an accuracy of $\pm 0.01 \text{ kgm}^{-3}$. An Oswald viscometer (10 ml) was used for the viscosity measurement with an accuracy of $\pm 0.001 \text{ Nsm}^{-2}$.

Parameters

Following parameters were calculated from the above measurements of ultrasonic velocity, density and

viscosity at different temperatures.

Adiabatic compressibility :

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

Where ' ρ ' is density and ' U ' is the ultrasonic velocity.

Intermolecular free length :

$$L_f = K_T \cdot \beta^{\frac{1}{2}} \quad (2)$$

Where, $K_T (= (93.875 + 0.375 \cdot T) \times 10^{-8})$ is Jacobson's temperature dependent constant and ' β ' is the adiabatic compressibility.

Free Volume :

$$V = \left(\frac{M_{eff} \cdot U}{K \cdot \eta} \right)^{\frac{3}{2}} \quad (3)$$

Where ' M_{eff} ' is the effective mass of the mixture, ' K ' is a dimensionless constant independent of temperature and liquid. Its value is 4.281×10^9 and ' η ' is the viscosity.

Surface tension :

$$S = 6.3 \times 10^{-4} \cdot \rho \cdot U^{\frac{3}{2}} \quad (4)$$

Results and Discussion

The experimental data of density, viscosity and ultrasonic velocity of three liquid mixtures at different temperatures are shown in Table 1. The calculated values of adiabatic compressibility, free length, free volume and surface tension are presented in Tables 2 and 3. Variations of adiabatic compressibility, with mole fraction of DMF for three mixtures are graphically represented in figs. 1, 2 and 3.

Both benzene and cyclohexane are non-polar, but benzene has a relatively higher dielectric constant. Hence

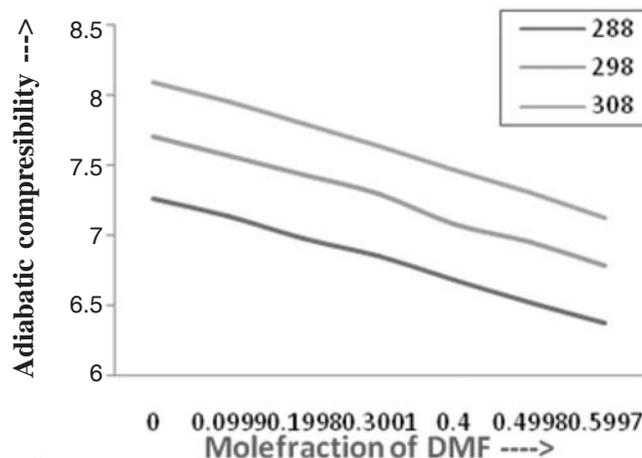


Fig. 1 Variation of adiabatic compressibility with mole fraction of DMF for mixture-I.

Table 1 – Values of density (ρ), viscosity (η) and velocity (U) at 288 K, 298 K and 308 K.

Mole fraction		Density (ρ) kgm^{-3}			Viscosity (η) (10^{-3} Nsm^{-2})			Velocity (U) ms^{-1}		
X_1	X_3	288 K	298 K	308 K	288 K	298 K	308 K	288 K	298 K	308 K
SYSTEM - I: (N, N-DMF + CYCLOHEXANE + BENZENE)										
0.0000	0.6000	835.26	830.94	824.87	0.912	0.680	0.536	1283.8	1250.4	1224.5
0.1998	0.4001	850.26	843.41	837.55	0.935	0.694	0.553	1298.4	1262.8	1237.4
0.4000	0.1999	862.86	856.25	850.61	0.959	0.719	0.574	1316.8	1284.5	1254.7
0.5997	0.0000	875.45	869.38	863.96	0.973	0.747	0.595	1338.7	1301.7	1274.4
SYSTEM - II: (N, N-DMF + CYCLOHEXANE + TOLUENE)										
0.0000	0.6000	816.85	814.56	811.76	0.804	0.653	0.538	1311.20	1269.4	1221.2
0.1998	0.4001	832.67	830.45	827.64	0.848	0.688	0.566	1329.4	1286.0	1241.5
0.4000	0.1999	852.56	849.64	845.54	0.916	0.756	0.632	1317.6	1267.7	1226.7
0.5997	0.0000	875.45	869.38	863.96	1.179	0.962	0.795	1283.5	1242.4	1192.5
SYSTEM - III: (N, N-DMF + CYCLOHEXANE + PYRIDENE)										
0.0000	0.6000	887.56	882.59	876.93	1.04	0.83	0.69	1330.2	1290.5	1265.4
0.1998	0.4001	881.98	877.93	869.49	1.09	0.87	0.73	1339.4	1298.3	1273.6
0.4000	0.1999	874.53	872.35	862.98	1.14	0.93	0.76	1348.5	1305.6	1280.6
0.5997	0.0000	865.69	858.61	849.65	1.18	1.01	0.81	1356.8	1314.2	1288.8

dispersive types of interactions are expected between them. DMF is a polar molecule. When it mixed with benzene and cyclohexane, the DMF-DMF dipolar association tends to breakdown, releasing several DMF dipoles. These free dipoles of DMF induce moments in the neighboring cyclohexane and benzene molecules which results in induced dipolar interaction.

It is observed from Table I for mixtures-I and III that, at a fixed temperature, with increase in concentration of DMF, velocity increases which may be due to the structural changes occurring in the mixture resulting in increase of intermolecular forces. However, when temperature increases, the intermolecular distance increases, resulting in decrease of the intermolecular forces and hence velocity.

Adiabatic compressibility decreases with increasing concentration of DMF, which is in conformation with the above fact. Compressibility gives the ease with which a medium can be compressed. In this case the medium appears to be more compact. This is also confirmed by the decreasing trend of free length¹¹. For mixtures-II, it is observed that, ultrasonic velocity increases as concentration of DMF increases and that of toluene decreases. When concentration of Toluene and DMF are equal, it becomes maximum and then decreases. This may be due to the fact that, as concentration of DMF increases, due to lack of perfect symmetry, (as DMF molecules have a aliphatic structure) the available space between the component molecules increases.

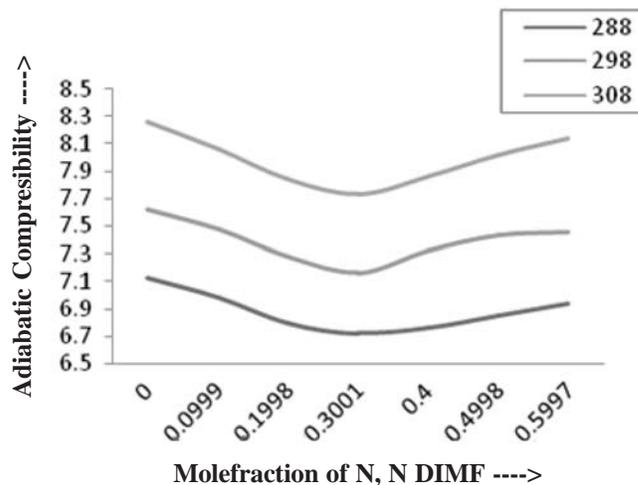


Fig. 2 Variation of adiabatic compressibility with mole fraction of DMF for mixture-II.

The increase in concentration of DMF results in decrease in free length and adiabatic compressibility. This trend is an indication of clustering together of the molecules as the associative effect of the polar group dominates over the other type of interaction. Free length, adiabatic compressibility and velocity show a reverse trend as temperature is increased. This happens as the spacing between the molecules increases leading to a less ordered structure. It is observed from Table 2 that, for all the mixtures, free volume decreases with increase in mole fraction of DMF. Intermolecular interaction seems to be stronger than the intra-molecular interaction which leads to a decrease of free volume. When

Table 2 – Calculated values of adiabatic compressibility (β) and Free Length (L_f).

Mole fraction		Adiabatic compressibility (β)			Free Length (L_f)		
X_1	X_3	288 K	298 K	308 K	288 K	298 K	308 K
SYSTEM - I: (N, N-DMF + CYCLOHEXANE + BENZENE)							
0.0000	0.6000	7.264	7.697	8.085	0.5283	0.5494	0.5747
0.1998	0.4001	6.976	7.435	7.798	0.5178	0.5400	0.5644
0.4000	0.1999	6.684	7.078	7.468	0.5068	0.5269	0.5523
0.5997	0.0000	6.374	6.788	7.127	0.4949	0.5160	0.5396
SYSTEM - II: (N, N-DMF + CYCLOHEXANE + TOLUENE)							
0.0000	0.6000	7.121	7.619	8.260	0.5231	0.5466	0.5809
0.1998	0.4001	6.795	7.281	7.839	0.5110	0.5344	0.5659
0.4000	0.1999	6.756	7.324	7.859	0.5095	0.5359	0.5666
0.5997	0.0000	6.934	7.452	8.139	0.5162	0.5406	0.5766
SYSTEM - III: (N, N-DMF + CYCLOHEXANE + PYRIDENE)							
0.0000	0.6000	6.367	6.803	7.122	0.4947	0.5165	0.5394
0.1998	0.4001	6.320	6.758	7.090	0.4928	0.5148	0.5382
0.4000	0.1999	6.288	6.725	7.066	0.4916	0.5135	0.5373
0.5997	0.0000	6.275	6.743	7.086	0.4910	0.5142	0.5380

Table 3 – Calculated values of Free volume (V_f) and Surface tension (S).

Mole fraction		Free volume (V_f)			Surface tension (S)		
X_1	X_3	288 K	298 K	308 K	288 K	298 K	308 K
SYSTEM - I: (N, N-DMF + CYCLOHEXANE + BENZENE)							
0.0000	0.6000	1.362	2.035	2.814	24205.2	23146.4	22267.1
0.1998	0.4001	1.311	1.967	2.679	25061.4	23844.1	22967.6
0.4000	0.1999	1.265	1.876	2.538	25975.3	24833.7	23816.7
0.5997	0.0000	1.243	1.773	2.414	27014.5	25722.7	24762.4
SYSTEM - II: (N, N-DMF + CYCLOHEXANE + TOLUENE)							
0.0000	0.6000	1.972	2.567	3.239	24433.5	23209.3	21824.7
0.1998	0.4001	1.741	2.266	2.881	25427.1	24127.7	22808.8
0.4000	0.1999	1.428	1.798	2.239	25688.6	24160.2	22886.7
0.5997	0.0000	0.875	1.130	1.415	25361.0	23985.1	22414.1
SYSTEM - III: (N, N-DMF + CYCLOHEXANE + PYRIDENE)							
0.0000	0.6000	1.193	1.599	2.049	27127.7	25777.2	24868.4
0.1998	0.4001	1.099	1.470	1.859	27237.3	25874.0	24897.4
0.4000	0.1999	1.014	1.311	1.724	27283.0	25926.7	24915.0
0.5997	0.0000	0.950	1.143	1.546	27256.9	25770.8	24766.2

temperature increases free volume increases. With increase in temperature, there is a reduction in molecular interaction as they move away from each other. This reduces the cohesive force. Thus, an increase in free volume occurs with increase in temperature.

From Table 3, it is observed that, surface tension in all the mixtures decreases with increase of temperature and increases comparatively slowly with increase in concentration of DMF. At a particular temperature, surface tension is maximum for the mixture-III and minimum for mixture-II, indicating the difference in

intermolecular interaction in the different mixtures. Surface tension of mixture-II is minimum indicate weakest interaction between the molecules.

Conclusion

It is obvious that, there exist a molecular interaction between the components of the mixture. In specific weak molecular interaction (like dipole-dipole, dipole-induced dipole and dispersive forces) are found to exist between components of the individual mixtures.

Acknowledgements

I am thankful to management of Ajay Binay Institute of Technology, CDA, Sector-1, Cuttack, Odisha, for providing the laboratory for the improvement of research activities in the Institute. I am also thankful to Dr. (Mrs.) Sarmistha Mishra for her guidance to make this work successful.

References

- 1 **Praharaj M.K.** and **Mishra S.**, Ultrasonic study of certain binary mixtures in terms of the excess values of thermodynamic parameters. *Int. J. Rec. Sci Res.*, **7** (2016) 9125-9128.
- 2 **Nath G.** and **Paikaray R.**, Effect of frequency on acoustic parameters in a binary mixture of polar liquids, *Ind. J. Phys.*, **83** (2009) 1567-1574.

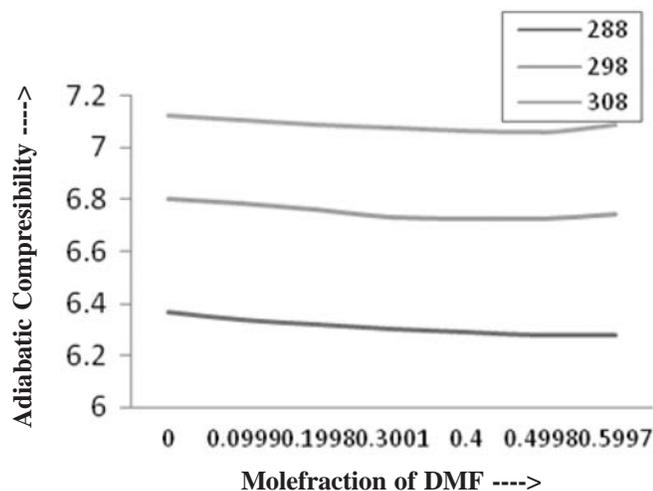


Fig. 3 Variation of adiabatic compressibility with mole fraction of DMF for mixture-III.

- 3 **Praharaj M.K.** and **Mishra S.**, Study of acoustic and thermodynamic parameters for binary mixture containing cyclohexane and the substituted benzenes at different temperatures, *J. Chem. Bio. Phy. Sc., Section C*, **5** (2014) 686-699.
- 4 **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.
- 5 **Praharaj M.K.**, **Satapathy A.**, **Mohanty J.** and **Mishra S.**, Thermodynamic parameters and their excess values for binary mixtures of cyclohexane plus benzene and substituted benzenes at different ultrasonic frequencies, *Int. J. Eng. Res. Tech.*, **3** (2014) 1060-1065.
- 6 **Praharaj M.K.** and **Mishra S.**, Molecular interaction in ternary liquid mixtures at different temperatures, *World J. Pharm. Pharmace. Sc.*, **5** (2016) 1597-1607.
- 7 **Dash A.K.** and **Paikaray R.**, Studies on acoustic parameters of ternary mixture of dimethyl acetamide in acetone and isobutyl methyl ketone using ultrasonic and viscosity probes, *Int. J. Chem. Phy Sc.*, **3** (2014) 69-79.
- 8 **Praharaj M.K.**, **Satapathy A.**, **Mishra P.** and **Mishra S.**, Ultrasonic Studies of Molecular Interactions in pyridine + N-N dimethylformamide + cyclohexane Ternary Liquid Mixtures at Different Temperatures, *J. Theo. Appl. Phys.*, **7** (2013) 1-6.
- 9 **Praharaj M.K.** and **Mishra S.**, Comparative study of molecular interaction in ternary liquid mixtures of polar and non-polar solvents by ultrasonic velocity measurements, *Int. J. Sci. Res.*, **3** (2014) 642-646.
- 10 **Praharaj M.K.**, **Satapathy A.**, **Mishra P.** and **Mishra S.**, Study of molecular interaction in mixture of n, n-dimethylformamide, cyclohexane and benzene for different frequencies of ultrasonic waves, *Golden Res. Thoughts*, **2** (2013) 1-10.
- 11 **Praharaj M.K.**, **Satapathy A.**, **Mishra P.** and **Mishra S.**, Ultrasonic analysis of intermolecular interaction in the mixtures of benzene with n, n-dimethylformamide and cyclohexane at different temperatures, *J. Chem. Pharm. Res.*, **5** (2013) 49-56.

Short Communication

Ultrasonic absorption of guanine in acidic solution

P. D. Bageshwar¹, O. P. Chimankar² and N. R. Pawar^{3,*}

¹Department of Physics, Mungsaji Maharaj Mahavidyalaya, Darwha - 445 304, India

²Department of Physics, RTM Nagpur University, Nagpur - 440 033, India

³Department of Physics, Arts, Commerce and Science College, Maregaon - 445 303, India

*E-mail: pawarsir1@gmail.com

Ultrasonic absorption of guanine in 10% HCl in distilled water by ultrasonic technique is essential for utilizing them in biomedical technology. In biological sciences, nitrogenous bases are increasingly termed nucleobases because of their role in nucleic acids, their flat shape is particularly important when considering their roles as the building blocks of DNA and RNA. The present paper reports the ultrasonic absorption and thermo-acoustic analysis of guanine in 10% HCl in distilled water by ultrasonic technique at different molar concentrations and temperatures. The non-linear and complex behaviour of guanine in partly acidic medium helps to detect phase separation and strength of intermolecular interactions between the constituents in the partly acidic solution of guanine.

Keywords: Ultrasonic absorption; guanine; Nomoto's relation.

Introduction

Ultrasonic wave velocity in a medium provides valuable information about the physical properties of the medium¹⁻³. It also provides important information about various inter and intra-molecular processes such as relaxation of the medium or the existence of isomeric states or the exchange of energy between various molecular degrees of freedom⁴⁻⁶. Ultrasonic parameters are extensively being used to study molecular interactions in pure liquids, binary liquid mixtures and ionic interactions in single and mixed salt solutions of bio-liquids⁷⁻⁸. The experimental investigations of ultrasonic absorption have shown that it provides a better insight into molecular processes.

Experimental

Materials and Methods

The liquids used were of BDH analar grade and were redistilled in the laboratory. In this study the measurements have been made in the temperature range 293 K-308 K. The temperature of the liquid mixture was kept constant by the use of thermostat U-10 with ± 0.01 K accuracy. Density measurement was carried out

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

Results and Discussion

Figure 1 shows the plot of experimental ultrasonic absorption (α/f^2) versus molar concentration of 10% HCl in distilled water at different temperatures 293K, 298K, 303K, 308K and 313K

It is observed that the ultrasonic absorption (α/f^2) increases with increase in the molar concentration of guanine in 10% HCl in distilled water.

It is clearly seen that smaller the temperature, greater the ultrasonic absorption. It is also observed that ultrasonic absorption (α/f^2) increases with increase in the molar concentration of guanine in HCl, indicating more stability of guanine molecules. Guanine molecule has two resonating structure which increases the relaxation time and hence ultrasonic absorption in this

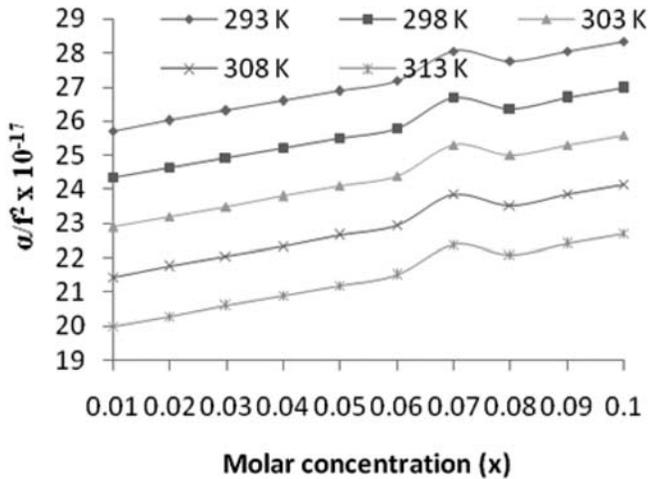


Fig. 1 Ultrasonic absorption versus conc. of acidic solution of guanine at different temperature.

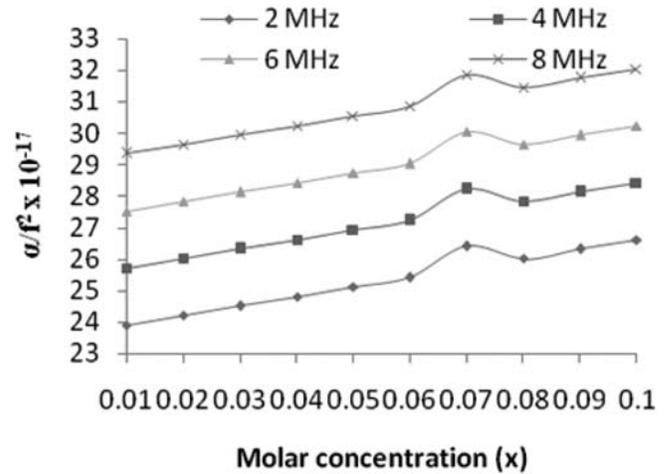


Fig. 2 Ultrasonic absorption versus conc. of acidic solution of guanine at different frequency.

binary liquid system. The non-linear variation of ultrasonic absorption in each curve with molar concentration strongly supports the presence of strong intermolecular interaction through hydrogen bonding and dipole-induced dipole interactions. The propagation of ultrasonic wave through binary liquid mixture disrupts thermal and structural equilibrium of the solution and produces energy transfer between different modes of the molecules. In this system structural relaxation plays a predominant role over thermal relaxation process. The viscosity of this binary system is also responsible for increase in ultrasonic absorption. From the Graph it is clear that, the remarkable peak is observed at molar concentration 0.07. This shows that, the constituent's molecules are more stable hence absorbs more ultrasonic energy.

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

It is observed that the ultrasonic absorption (α/f^2) increases with increase in the molar concentration of guanine in 10% HCl in distilled water.

It is clearly seen that smaller the frequency, smaller the ultrasonic absorption. It is also observed that ultrasonic absorption (α/f^2) increases with increase in the molar concentration of guanine in 10% HCl in distilled water, indicating more stability of guanine molecules. Guanine molecule has two resonating structure which increases relaxation time and stability of guanine molecules hence increases ultrasonic absorption.

The non-linear variation of ultrasonic absorption in each curve with molar concentration strongly supports the presence of strong intermolecular interaction through hydrogen bonding and dipole-induced dipole interactions. The hydrogen bonding exists between nitrogen atom of guanine and hydrogen atom of HCl in the medium. The viscosity of this binary system is also responsible for increase in ultrasonic absorption. From the Graph it is clear that, the remarkable peak is observed at molar concentration 0.07. This shows that, the constituent's molecules are more stable hence absorbs more ultrasonic energy.

Figure 3 shows the comparison of experimental ultrasonic velocity with theoretical values computed by empirical Impedance Dependence Relation (IDR) and Nomoto's relation. It is observed that experimental ultrasonic velocity in 10% HCl solution of guanine are

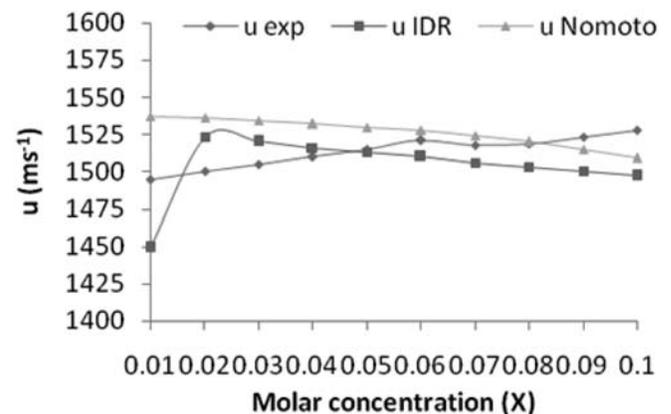


Fig. 3 Ultrasonic velocity versus concentration.

in good agreement with the values produced by empirical impedance dependence relation (IDR) and Nomoto's relation.

Conclusion

- The non-linear variation of ultrasonic absorption in each curve with molar concentration strongly supports the presence of strong intermolecular interaction through hydrogen bonding and dipole-induced dipole interactions.
- Structural relaxation plays a predominant role over thermal relaxation. Increase in ultrasonic absorption with molar concentration is due to possible structural relaxation process.
- The viscosity of this binary system is responsible for increase in ultrasonic absorption.

References

- 1 **Nayeema S.M. and Rao D.K.**, Ultrasonic investigations of molecular interaction in binary mixtures of benzyl benzoate with isomers of butanol, *Int. J.P. Res. Rev.* **3**(2014) 65-78.
- 2 **Singh D., Bhalla V., Bala J. and Wadhwa S.**, Ultrasonic investigations on polonides of Ba, Ca and Pb, *Z. Naturforsch.* **72**(2017) 977-983.
- 3 **Tripathy C., Singh D. and Paikaray R.**, Behaviour of elastic and ultrasonic properties of curicum monopnictides, *Can. J. Phys.*, **96**(2018) 513-518.
- 4 **Pawar N.R. and Chimankar O.P.**, Comparative study of ultrasonic absorption and relaxation behavior of polar solute and non-polar solvent, *J. Pure Appl. Ultrason.*, **34**(2012) 49-52.
- 5 **Mehra R., Pancholi M. and Gaur A.K.**, Ultrasonic and thermodynamic studies in ternary liquid system of toluene+1-dodecanol+cyclohexane at 298, 308 and 318 K, *Arch Appl Sci Research*, **5**(2013) 124-133.
- 6 **Panwar N.R.**, Ph.D. thesis summary on investigation of Ultrasonic were absorption in some Bio-liquids, *J. Pure Appl. Ultrason.*, **36**(2014) 69-70.
- 7 **Janankar G.M. and Pandey M.S.**, Ultrasonic investigations of molecular interaction in bianary mixtures of ellagic acid with acetone, *J. Pure Appl. Ultrason.*, **40**(2018) 12-15.
- 8 **Mathana Gopal A. and Poongodi J.**, Study of thermodynamic properties in binary liquid mixtures through ultrasonic measurement, *J. Pure Appl. Ultrason.*, **39**(2016) 122-126.

Ph.D. Thesis Summary

Ultrasonics and Thermophysical Properties of Nanoparticles-Based Engineering Materials

(Awarded in 2017 by University of Allahabad, Allahabad to Dr. Punit Kumar Dhawan, Department of Physics, University of Allahabad, Allahabad, UP, India- 211002)

The Ph.D. thesis is focused to ultrasonic and thermophysical properties characterization of nano-structured materials like semiconducting nanowires, thermoelectric nanowires, magnetic nanoparticles and conducting polymer/novel metal nanocomposites. When propagated in different material systems, ultrasonic waves are influenced by the microstructure, nanostructures, deformation process, structural inhomogeneities, non linear thermal/ physical properties, strength of the materials, phase transformations, reinforcement level of particles (nanofibers, nanorods, nanotubes *etc.*) in nanocomposites, size of the particles and their distribution in the liquid/solid phase matrix and various surface morphology/phenomena.

Mechanical, thermal and many other interesting properties at different physical conditions like temperature, pressure, crystallographic orientations, size and shape of the particles and their distribution in liquid/solid phase matrix are well related to ultrasonic attenuation and velocity along with the associated scientific parameters. Thus, ultrasonic waves can be used to detect and examine the usual and unusual properties at any stage of production of the materials.

In view of the above, the principal objective of the thesis is to establish the growth technology of the nanostructures the nanofluids/nanocomposites based on the different shaped suspended nanoparticles. Further, the second objective is to establish/develop the ultrasonic mechanism/method to extract useful, important information about the nanostructures and temperature dependent thermophysical properties. For that, simple interaction potential model for the calculation of non linear elastic constants has been established which is needed to determine ultrasonic attenuation and related parameters. Important

correlations have been established to investigate complete characteristics. Also the microscopic characterizations such as TEM, SEM, *etc.* are followed for the comparison/correlations.

The diameter dependent thermal conductivity and total ultrasonic attenuation over frequency square has been calculated. Other associated parameters like thermal relaxation time, thermal energy density, longitudinal and shear ultrasonic velocity and acoustic coupling constants have also been studied. Importance has been given to temperature, surface roughness and diameter of nanowires dependent study of the properties of the materials. Surface roughness dependent total ultrasonic attenuation gives valuable information about the materials which are very useful for thermoelectric device applications. The temperature dependent ultrasonic properties of thermoelectric nanowires PbTe have been calculated. Temperature dependent ultrasonic attenuation has also been studied. Further, the experimental study of Polyaniline/Cu nanocomposites and cobalt ferrite (CoFe_2O_4) nano-particles and its DI-water suspension have been made. Temperature dependent thermal conductivity of PANI/Cu nanocomposites was measured in a wide temperature range 0 to 100°C for two different concentrations of the nanocomposites. Temperature dependent and concentration dependent thermal conductivity data can be utilized in thermal management required for optical/electronic industries. Further the dielectric properties of nanocomposites were recorded in a wide frequency range 1 Hz to 1 MHz. The enhancement of the dielectric constant in the Cu/PANI nanofibers is because of interfacial polarization between PANI and copper nanofibers. The determined dielectric properties are important in energy storage systems. Electrical conductivity of synthesized material has also been

studied and appreciable increment is recorded in PANI/Cu nanocomposites in comparison to pristine PANI. The synthesis and characterization of cobalt ferrite nanoparticles and its DI-water suspension have been investigated. The synthesized material has been subjected to different structural and morphological characterization and it shows the uniform dispersion of nanoparticles in DI-water and cubical structure formation of CoFe_2O_4 NPs. Magnetic property of synthesized material shows that the material is ferromagnetic in nature. And the coercivity of the sample was found as 1735 Oe, while saturation magnetization and remanent magnetization was recorded as 46 emu/g and 16 emu/g respectively. The results may be used for magnetic industrial/scientific applications. Transient plane source method to determine the temperature dependent thermal conductivity of the CoFe_2O_4 nanoparticles is established. Thermal conductivity remains almost

constant with temperature with theoretical justifications. Particle size distribution study was done by ultrasonic APS-100 study and it shows that maximum particles are distributed between 20-25 nm. The result is compared with TEM characterization and it was found that both results are comparable. The ultrasonic velocity of the synthesized nanofluid of DI-water suspended CoFe_2O_4 nanoparticles were measured using Ultrasonic Interferometer method. The ultrasonic velocity of nanofluid shows increasing behaviour with temperature extracting the information about viscoelasticity/elastic component of the nanofluids.

In view of above we have made the important predictions/experimental findings with justified theoretical approach about the interesting properties as the basics of the analytical study. The conclusions were made aiming their use in scientific and advanced industrial applications.

Inauguration of USI Student Chapter- Thiagarajar College, Madurai-625009

The inauguration of the Student Chapter of Ultrasonics Society of India by the Department of Physics, Thiagarajar College was held on 11.01.2018.

Dr. R. Vijayalakshmi, Associate Professor and Head of the Department of Physics, Thiagarajar College, welcomed the gathering.



Mr. Karumuttu K. Thiagarajan, Secretary, Thiagarajar College, offered the inaugural address and spoke about the importance of 'interconnection' among subjects of science and arts citing examples from Tamil scriptures and life of the ancient Avvaiyar. He also insisted upon the importance of practical application of acquired knowledge as a survival skill. He further emphasized the interdisciplinary nature of the field of ultrasonics which finds application in various fields such as medicine, engineering, science, *etc.*

Dr. P. Palanichamy, retired Scientist, IGCAR, Kalpakkam and former Vice-President, Ultrasonics Society of India, delivered a special lecture on the applications of ultrasonics highlighting career opportunities for students. He explained the basic principle of ultrasonics and its importance in the field of nuclear industry, particularly ensuring defect free vessels for nuclear reactors. He also elaborated on the various opportunities available through the Ultrasonic Society and insisted that students avail them to enhance their future job and research prospects.

Dr. J. Poongodi, Executive Council Member,

Ultrasonics Society of India and Associate Professor of Physics, Kamaraj College, Tuticorin, offered felicitations. Dr. Poongodi narrated her fruitful experiences as the member of USI since her student days, how they stimulated research interest in the field of ultrasonics and provided her scope to become the Executive Council Member of the USI.

Dr. D. Pandiaraja, Principal, Thiagarajar College, in his felicitation address, inspired students to take up research in the field of ultrasonics and explore new avenues in taking its benefits to the society.

The event was organized by Dr. S. Rajakarthishan, Assistant Professor of Physics, Thiagarajar College, who is also Life Member of the Ultrasonics Society of India. Dr. N. Srinivasan, Associate Professor, Department of Physics, Thiagarajar College, delivered the vote of thanks.

On the day of inauguration around 25 student members were enrolled in the student chapter. Faculty members and students from other departments and colleges participated.

Forthcoming Events

1. The 6th International Symposium on Laser Ultrasonics (LU-2018), 9-13 July, 2018, University of Nottingham, UK
2. International Congress on Sound and Vibration, 8-12 July, 2018: Hiroshima, Japan
3. Internoise 2018, 26-29 August, 2018: Chicago USA
4. Greenbuild 2018, 14-16 November: Chicago, USA
5. IEEE International Ultrasonics Symposium, 22-25 October, 2018, Kobe, Japan
6. 13th WESPAC 2018, 11-15 November 2018, CSIR-NPL, New Delhi, India
7. 2019 International Congress on Ultrasonics (ICU), 3-6 September, 2019, Bruges, Belgium

Journal of Pure and Applied Ultrasonics

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

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.