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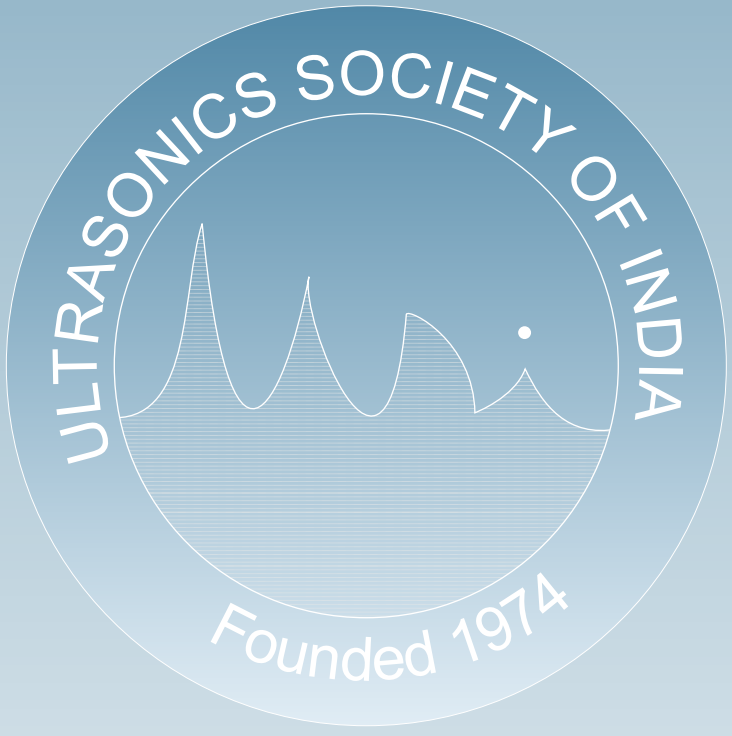

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Thermoacoustical analysis of binary mixtures of N-N-dimethyl formamide (DMF) with BAE and 1-BuOH

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Ultrasound techniques are unique and find wide applications and acceptance in all fields. Applications of ultrasonic have made possible not only the evaluation of physico-chemical properties of the mixtures/ solutions but also more reliability on the interpretation of molecular interactions. In view of the wide scope of molecular interactions between the highly polar compound of N-N-dimethylformamide with butylaminoethanol and 1-butylalcohol, ultrasonic velocity and densities have measured for these systems over the whole composition range at temperatures 293.15K, 298.15K, 303.15K, 308.15K and 313.15K under atmospheric pressure. To gain some insight into the several aggregations of molecular interactions present in these mixed solvents, deviation in ultrasonic velocity, excess acoustic impedance and excess pseudo Grüneisen parameter have been predicted. A qualitative analysis of the results is discussed in terms of the ion-dipole, ion-pair interactions, dispersive forces and hydrogen bonding prevailing in the binary mixtures. Further experimental data of these mixtures were also used to test the validity of various mixing rules/ theory for ultrasonic velocity.

Keywords: Ultrasonic, molecular interactions, thermophysical, deviation in velocity, excess Pseudo Grüneisen parameter.

Introduction

The ultrasonic and thermodynamic studies of liquid and liquid mixtures are fascinating and of high fundamental, practical importance in industry and used extensively in manufacturing process control, chemical processing and many other significant fields. The ultrasonic velocity measurements are highly sensitive to molecular interactions and have been particularly informative in elucidating the solute-solute and solute-solvent interactions prevailing in the mixtures through physical nature and strength of the molecular interactions in the liquid mixtures[1-2]. The anatomy relying of thermodynamic properties is an effective tool in assimilating the nature and magnitude of pattern of molecular aggregation resulting from intermolecular interactions within the components. The ultrasonic velocity and density study provides valuable information in predicting the type of interactions prevailing in the liquid mixtures.

DMF (N-N dimethylformamide, $(CH_3)_2NCHO$) is a hydrophilic aprotic solvent with high boiling point, widely used in variety of industrial process[3, 4]. DMF molecule has a planar skeletal geometry and is of particular interest because any significant structural effects are absent due to lack of hydrogen bonds, it may be applied as an aprotic protophilic solvent with a large dipole moment and a high dielectric constant ($\mu = 3.24$D and $\varepsilon = 36.71$ at 26°C)[5]. It can dissolve wide range of both organic and inorganic substances because of its good donor- acceptor properties. The resonance structure of DMF is shown in Fig. 1.

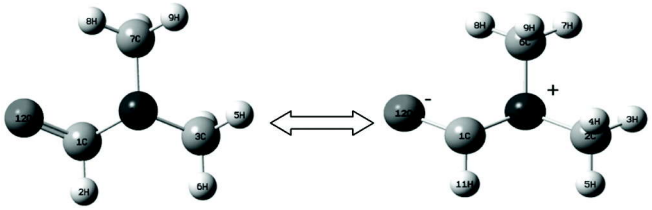

Fig. 1 Resonance structure of DMF.

The negative pole oxygen atom juts out from the molecule and is the best hydrogen acceptor whereas positive pole nitrogen atom is buried within the molecule and the presence of two replling $-CH_3$ groups compel

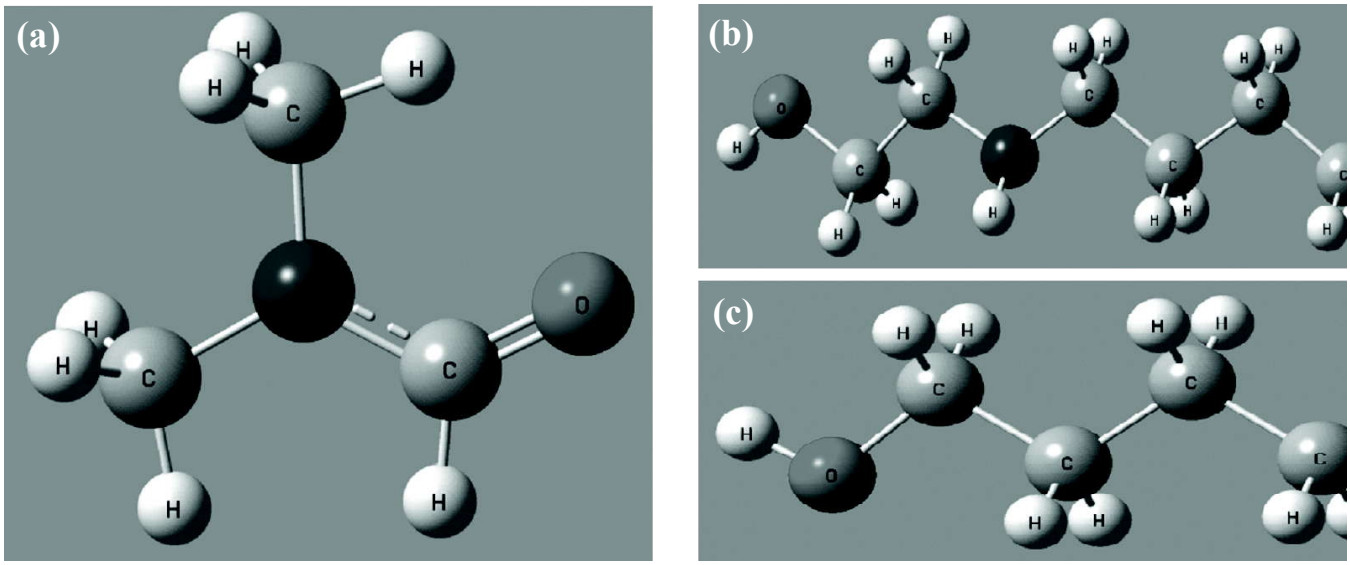

Fig. 2 Schematic structure of (a) DMF (b) BAE (c) 1-BuOH with 6-31+ G basis set using Gaussian 09 software.

the lone pair at the nitrogen for donation[6-7]. The schematic optimized chemical structures of DMF as well as butylaminoethanol (BAE) and 1-butylalcohol (1-BuOH) using basis set 6-31 +G are shown in Fig. 2.

In the present work ultrasonic velocity *(u)* and density *(ρ)* have been measured for the binary mixtures DMF with BAE and 1-BuOH. To characterize the type and magnitude of molecular interactions between DMF and BAE/1-BuOH deviation in ultrasonic velocity *(Δu)*, excess acoustic impedance (Z^E) and excess Pseudo Grüneisen parameter (Γ^E) have been evaluated at temperatures 293.15K, 298.15K, 303.15K, 308.15K and 313.15K and at atmospheric pressure over the full composition range. Further, different semi-empirical relations and theory such as Nomoto's, Vandeal and Vangeel's, Junjie's, Schaff's and Flory statistical theory (FST) have been applied to these systems under to analyze and verify applicability of these relations/ theories.

Experimental

Materials

N-N Dimethyformamide (molecular weight Mn = 73.09), Butylaminoethanol (BAE) (molecular weight Mn= 117.19) and 1-Butylalcohol (1-BuOH) (molecular weight Mn= 74.12) have been obtained from Sigma Aldrich Chemicals Pvt. Ltd. and no further purification was done (Table 1).

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. A 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.

Table 1 – Materials Description in the work

Chemical name	Source	CAS Number	Purity	Linear Formula
N-N Dimethylformamide	Sigma Aldrich	68-12-2 (puriss.p.a, ACS reagent)	≥ 99.8% (GC)	$HCON(CH_3)_2$
2- (Butylamino)ethanol	Sigma Aldrich	111-75-1	≥ 98%	$CH_3(CH_2)_3NHCH_2CH_2OH$
1-Butylalcohol	Sigma Aldrich	71-36-3 (ACS reagent)	≥ 99.40%	$CH_3(CH_2)_3OH$

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. The 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 2MHz. 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%. Uncertainty of ultrasonic interferometer is ±0.5 m.

The density of each liquid mixture has been measured using a pycnometer. The pycnometer consists of a long tube graduated in 0.01 ml scale, fitted to a specific gravity bottle of capacity 8 ml. A certain mass of the solution is allowed to expand at the desired temperature and the densities were calculated from the fixed mass and the volume at various temperature. Pycnometer was immersed vertically in a doubled walled cylindrical water jacket. The liquid rise in the capillary of pycnometer was measured by travelling microscope (having a least count of 0.001 cm) for accuracy. The precision of the measured densities is of the order of $\pm 1 \times 10^{-4}$ g cm^{-3} and with an uncertainty of ±0.0005 g cm^{-3}. An average of four to five measurements was taken for each sample mixtures.

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 ±0.01°C.

Results and Discussion

Experimental values of densities and ultrasonic velocities of the pure liquids at temperatures 293.15K, 298.15K, 303.15K, 308.15K and 313.15K are found to be in good agreement with literature values (Table 2). The experimental values of densities and ultrasonic velocities for binary mixtures DMF + BAE and DMF + 1-BuOH at temperatures 293.15K, 298.15K, 303.15K, 308.15K and 313.15K are given in Table 3.

Excess parameters

In order to understand the nature of molecular interactions between the components of liquid mixtures, it is of interest to discuss the same in terms of excess parameters. Excess properties provide information about the molecular interactions and macroscopic behavior of fluid mixtures. Non- ideal liquid mixtures show considerable deviation from linearity in their physical behavior with respect to concentration and these have

Table 2 – Comparison of density *(ρ)* and ultrasonic velocity *(u)* with literature data at different temperatures.

		Ultrasonic velocity, *u* (in m/s)		Density *(ρ)*	
Component	T/K	Literature	Experimental	Literature	Experimental
DMF	293.15K		1499.2	0.952[8]	1.01211
	298.15K		1478.8		0.99809
	303.15K	1459[8]	1458.8	0.9470[8]	0.99037
	308.15K	1439[9]	1432.4	0.9355[10]	0.98190
	313.15K	1415[10]	1408.8	0.9309[10]	0.97113
BAE	293.15K	-	1392.4	-	0.90199
	298.15K	-	1375.2	-	0.89617
	303.15K	-	1352.8	-	0.88966
	308.15K	-	1342.4	-	0.88529
	313.15K	-	1326.0	-	0.88061
1-BuOH	293.15K	1256[11]	1260.4	0.8098[11]	0.83531
	298.15K	-	1241.6	-	0.83050
	303.15K	1223[11]	1229.2	0.8017[12]	0.82287
	308.15K	-	1215.6	-	0.81258
	313.15K	1193[13]	1196.0	0.7934[14]	0.80461

Table 3 – The experimental values of densities and ultrasonic velocities for binary mixtures DMF + BAE and DMF + 1-BuOH at temperatures 293.15K, 298.15K, 303.15K, 308.15K and 313.15K.

DMF + BAE			DMF + Bu-OH		
X_1	u (m/s)	ρ (g/cm^3)	X_1	u (m/s)	ρ (g/cm^3)
			293.15K		
0.000000	1392.4	0.901997	0.000000	1260.4	0.83531
0.500064	1440.8	0.917716	0.499743	1374.4	0.87509
1.000000	1499.2	1.012118	1.00000	1499.2	0.99191
			298.15K		
0.00000	1375.2	0.896177	0.000000	1241.6	0.8305
0.500064	1409.8	0.912086	0.499743	1359.2	0.87030
1.00000	1478.8	0.998097	1.000000	1478.8	0.98431
			303.15K		
0.000000	1352.8	0.889662	0.000000	1229.2	0.82287
0.500064	1382.0	0.902707	0.499743	1342.6	0.86490
1.000000	1458.8	0.990372	1.000000	1462.8	0.97549
			308.15K		
0.000000	1342.4	0.885293	0.000000	1215.6	0.81258
0.500064	1359.8	0.897302	0.499743	1322.6	0.85856
1.000000	1432.4	0.981907	1.000000	1432.4	0.96577
			313.15K		
0.00000	1326.0	0.880611	0.000000	1196.0	0.80461
0.500064	1344.8	0.889504	0.499743	1303.2	0.85458
1.000000	1408.8	0.971139	1.000000	1418.8	0.96098

been interpreted as arising from the presence of strong and weak interactions. The effect of deviation depends upon the nature of the constituents and composition of the mixtures.

The most common way to evaluate the excess values[15] of a given thermodynamic parameter is to use the equation

$$A^E = A_{exp} - \Sigma x_i A_i \quad (1)$$

where A_{exp}, A_i and x_i are experimentally measured value of the parameter A, value of parameter a for i^{th} component ($i = 1, 2$ for binary mixture) and mole fraction respectively. A^E is deviation/ excess value of the respective parameter.

Deviation in ultrasonic velocity *(Δu)*, excess intermolecular free length (L_f^E), excess acoustic impedance *(Z^E)*, excess Pseudo-Grüneisen parameter *(Γ^E)* can thus be written as

$$\Delta u = u_m - (x_1 u_1 + x_2 u_2) \quad (2)$$

$$Z^E = (\rho_m u_m) - (x_1 \rho_1 u_1 + x_2 \rho_2 u_2) \quad (3)$$

$$\Gamma^E = \Gamma_m - (x_1 \Gamma_1 + x_2 \Gamma_2) \quad (4)$$

These excess properties are fundamentally important in understanding the intermolecular interactions and nature of molecular agitation in dissimilar molecules. These are found to be sensitive towards difference in size and shape of the molecules[16]. These functions give an idea about the extent to which the given liquid mixtures deviate from ideality.

Deviations in ultrasonic velocity is given in Tables 3-4 excess acoustic impedance and excess Pseudo-Grüneisen parameter have been reported in Figs. 3-4.

A perusal of Table 2-4 reveals that the values of deviation in ultrasonic velocity *(Δu)* are negative over the entire range of mole fraction of DMF for the systems DMF+BAE and DMF+1-BuOH. The sign and magnitude of deviation in ultrasonic velocity play 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[17-18]. The negative deviation in ultrasonic velocity may be due to the presence of dispersion forces and a positive deviation

in ultrasonic velocity may be due to charge-transfer, dipole-dipole and dipole - induced dipole interactions. The magnitude of Δu suggests that the interaction between DMF and 1-BuOH is strong as compared to DMF and BAE. Δu values are found to increase with increasing temperature for both the systems which indicate that strength of interaction increases with thermal energy.

A perusal of Fig. 3 shows the variation of excess acoustic impedance with increasing mole fraction of DMF. The values are found to be negative for both the systems DMF + BAE and DMF + 1-BuOH and at all the temperature suggesting the presence of weak interaction in both the system. The magnitude of Z^E interprets that interaction between DMF and 1-BuOH is strong as compared to that of DMF and BAE. Z^E values are found to increase with increasing temperature for both the systems which indicate that strength of interaction increases with thermal energy.

The Pseudo-Grüneisen parameter (Γ) is one of the most important parameter which is used to study the internal structure, clustering phenomenon and thermodynamic properties of solid crystalline lattice. It is well established that liquids support a quasi- crystalline model for their structure, the lattice nature being increased at high pressure and low temperature hence the Pseudo-Grüneisen parameter can also be used to study liquids. Fig. 4 shows that the excess Pseudo-Grüneisen parameter (Γ^E) of mixture increases with increase in mole fraction of DMF and are found to be positive for both the systems and decreases with rise in temperature for the systems DMF + BAE and DMF + 1-BuOH.

Computation of ultrasonic velocity using various mixing rules/ theories

Ultrasonic velocity of liquid and liquid mixtures has gained much importance during the last two decades in assessing the nature of molecular interactions and investigating the physicochemical behavior of such systems.

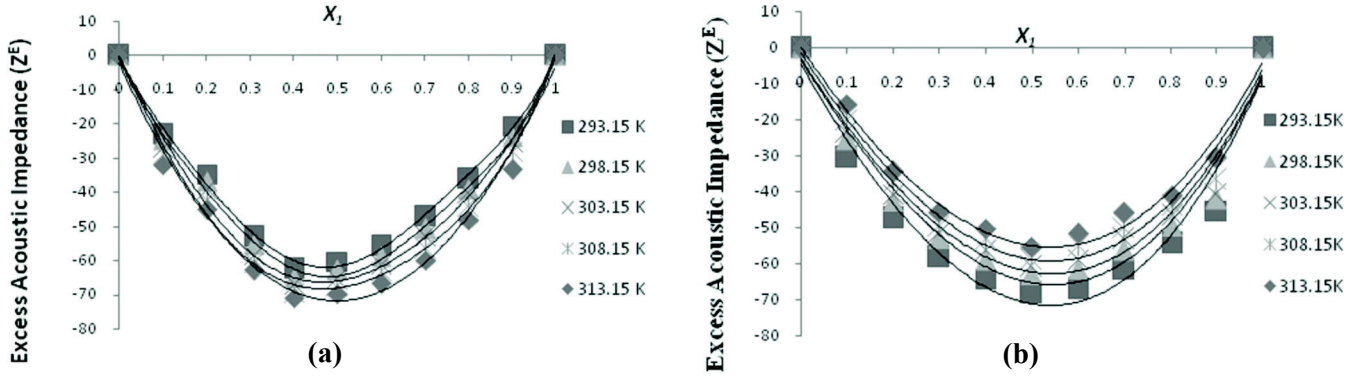

Fig. 3 Excess Acoustic Impedance (Z^E) verses the mole fraction of DMF (x_1) for binary mixtures: (a) DMF +BAE and (b) DMF + 1- BuOH at 293.15K, 298.15K, 303.15K, 308.15K and 313.15K.

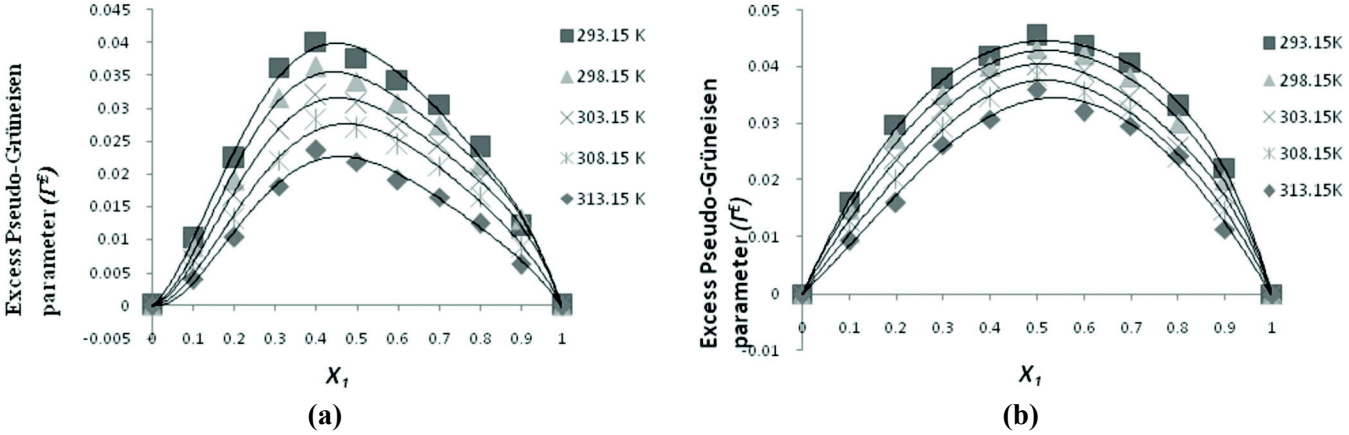

Fig. 4 Excess Pseodo Grunessian parameter (Γ^E) verses the mole fraction of DMF (X_1) for binary mixtures: (a) DMF +BAE and (b) DMF + 1- BuOH at 293.15K, 298.15K, 303.15K, 308.15K and 313.15K.

Table 4 – Ultrasonic velocity mixing rules for binary mixture DMF + BAE with mole fraction of DMF (x_1) at T = 293.15 K, 298.15 K, 303.15 K, 298.15 K and 313.15 K.

X_1	Experimental	FST	Nomoto	Vandeal	Junjie	Schaffs
			293.15K			
0.000000	1392.4	1376.863	1392.400862	1392.40000	1392.400	1392.4
0.500064	1440.8	1444.267	1440.801714	1415.71903	1423.049	1440.8
1.000000	1499.2	1454.189	1499.199990	1499.20000	1499.200	1499.2
			298.15K			
0.000000	1375.2	1373.168	1375.199320	1375.200000	1375.200	1375.2
0.500064	1409.8	1430.890	1409.801813	1397.199302	1405.509	1409.8
1.000000	1478.8	1449.618	1478.799725	1478.800000	1478.746	1478.8
			303.15K			
0.000000	1352.8	1364.644	1352.799473	1352.800000	1352.800	1352.800
0.500064	1382.0	1421.544	1381.999309	1376.681001	1383.848	1381.999
1.000000	1458.8	1444.214	1458.800102	1458.800000	1458.800	1458.800
			308.15K			
0.000000	1342.4	1366.070	1342.398586	1342.400000	1342.400	1342.399
0.500064	1359.8	1412.650	1359.800653	1357.735182	1369.071	1359.800
1.000000	1432.4	1432.931	1432.400274	1432.400000	1432.400	1432.400
			313.15K			
0.000000	1326.0	1361.938	1325.998685	1326.000000	1326.000	1325.999
0.500064	1344.8	1407.855	1344.800444	1337.757048	1350.923	1344.800
1.000000	1408.8	1423.909	1408.800036	1408.800000	1408.800	1408.800

Table 5 – Ultrasonic velocity mixing rules for binary mixture DMF + 1-BuOH with mole fraction of DMF (x_1) at T = 293.15 K, 303.15 K, and 313.15 K.

X_1	Experimental	FST	Nomoto	Vandeal	Junjie	Schaffs
			293.15 K			
0.000000	1260.4	1271.010	1260.400174	1260.400000	1260.400	1260.4
0.499743	1374.4	1387.262	1374.400051	1365.095937	1339.136	1374.4
1.000000	1499.2	1457.191	1499.200044	1499.200000	1499.200	1499.2
			303.15 K			
0.000000	1229.2	1263.625	1321.999757	1322.000000	1322.000	1322.0
0.499743	1342.6	1378.476	1379.199985	1358.066071	969.7492	1379.2
1.000000	1462.8	1449.536	1396.800204	1396.800000	358.1655	1396.8
			313.15 K			
0.000000	1196.0	1254.400	1280.399821	1280.400000	1280.400	1280.4
0.499743	1303.2	1362.720	1352.999758	1325.176996	1311.287	1353.0
1.000000	1418.8	1434.004	1374.400228	1374.400000	1374.400	1374.4

Nomoto assumed that linearity of the molar sound velocity and the additivity of the molar volumes in liquid solutions, gave the following relation

$$u_m = \left(\frac{R_m}{V_m}\right)^3 = \left(\frac{x_1R_1 + x_2R_2}{x_1V_1 + x_2V_2}\right)^3 \qquad (5)$$

Van Dael and Vangeel[22] proposed the following ideal mixing relation for predicting ultrasonic velocity of a binary liquid mixture

$$\left(\frac{1}{x_1M_1 + x_2M_2}\right)\frac{1}{u_m^2} = \left(\frac{x_1}{M_1u_1^2} + \frac{x_2}{M_2u_2^2}\right) \qquad (6)$$

Junjie[20] gave following relation for the ultrasonic velocity in a binary mixture

$$u_m = \frac{x_1V_1 + x_2V_2}{\sqrt{\left(x_1M_1 + x_2M_2\right)\left(\frac{x_1V_1}{\rho_1u_1^2} + \frac{x_2V_2}{\rho_2u_2^2}\right)}} \qquad (7)$$

Schaaffs' relation[21], which is based on the Collision Factor Theory (CFT), for predicting ultrasonic velocity in pure liquids, has been extended to the binary liquid mixtures by Nutsch-Kuhnkies[22] and is given as

$$u_m = u_{¥}\left(x_1S_1 + x_2S_2\right)\frac{\left(x_1B_1 + x_2B_2\right)}{V_m} \qquad (8)$$

The values of surface tension obtained by Flory theory have been used to evaluate sound velocity, making use of the well-known Auerbach relation[26].

$$u_m = \left(\frac{\sigma_m}{6.3\,\mathrm{X}10^{-4}\,\rho_m}\right)^{2/3} \qquad (9)$$

where *M, ρ, n, ϕ, w, u, σ, R, S, B* and *x* represent molecular weight, density, refractive index, volume fraction, weight fraction, ultrasonic velocity, surface tension, molar sound velocity, collision factior, actual volume of the molecule per mole and mole fraction of mixtures respectively. Symbols 1, 2 and m, in suffix represent pure components and mixtures respectively.

Table 6 reveals that for both the system average percentage deviation Vandeal and Junjie are in fairly good agreement with the experimental values with minimum average percentage deviation -0.02832 and -0.02833 for the system DMF+ BAE respectively and for the system DMF + 1-BuOH minimum average percentage deviation -0.85312.

Conclusion

The density (ρ) and ultrasonic velocity (u) of binary mixtures of DMF with BAE and 1- BuOH were measured at different temperatures. From the experimental data, various parameters, Δu, Z^E and Γ^E over the whole composite range were calculated. It may be concluded that the observed negative and positive values of various derived parameters show the presence of dispersive forces and weak hydrogen bonding between the binary mixtures DMF+ BAE and DMF + 1-Butanol. The magnitude of parameters interprets that interaction between DMF and 1-BuOH is strong as compared to that of DMF and BAE and values are found to increase with increasing temperature for both the systems which indicates that strength of interaction increases with thermal energy. The theories used for evaluation of the ultrasonic velocity, Vandeal and Junjie's show good agreement with the respective measured values of ultrasonic velocities for the systems DMF + BAE and DMF + 1-BuOH.

Acknowledgment

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Table 6 – Average Percentage values in the values of ultrasonic velocities evaluated from various methods of DMF + BAE and DMF + 1-BuOH mixtures at temperatures 293.15 K, 298.15 K, 303.15 K, 308.15 K and 313.15 K.

	ultrasonic velocites (m. s^{-1})				
T/K	FST	Nomoto	Vandeal	Junjie	Schaffs
			DMF+ BAE		
293.15K	0.70992	-1.47442	0.79458	0.79458	-7.91325
298.15K	-0.37557	-2.27804	0.23943	0.23943	-1.29548
303.15K	-1.86191	-1.72949	-0.02832	-0.02833	-4.22654
308.15K	-2.84236	1.55351	-0.44919	-0.44195	1.22445
313.15K	-3.63013	-2.88501	-0.32621	-0.32621	4.11548
			DMF+1-BuOH		
293.15K	2.54357	-1.44909	1.52342	1.52342	3.47719
298.15K	0.99215	-2.08063	-0.85312	-0.85312	-2.08063
303.15K	0.19428	-2.81034	-7.23965	-7.23965	-2.28103
308.15K	-0.47421	-2.41107	-1.02233	-1.02233	-2.41107
313.15K	-0.86227	-3.11709	-1.21936	-1.21936	-3.11710

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Study of enhancement of ultrasonic velocity in methanol based silver nanoparticle suspension

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In this study, the methanol-based nanofluids was prepared by synthesizing silver nanoparticles by thermal decomposition method and then dispersed Ag nanoparticles in pure methanol using magnetic stirring equipment. The main objective of this paper is to measure the acoustic and thermo physical parameters of the methanol-based nanofluids at different concentration and at different temperature. We have also measured the particle size, Miller indices and lattice parameters of silver nanoparticles. The multifrequency interferometer techniques at the frequency of piezoelectric transducers 1 MHz is applied for measuring the ultrasonic velocity of methanol-based nanofluids with an accuracy of ±0.1 m. The results show that ultrasonic velocity decreases initially with an increase of the nanoparticle weight/volume fraction, and then again increases and the enhancement is observed at concentration of 0.008 ?. Dipole-Induced dipole type of interaction and Agglomerisation of nanoparticles is considered to be the main reason for the ultrasonic velocity enhancement.

Keywords: Silver nanoparticles, XRD, ultrasonic velocity.

Introduction

Nanotechnology is the synthesis and applications of ideas from science and technology towards the understanding and production of novels materials. In the recent years, nanoparticle of metals exhibited significantly distinct physical, chemical, optical, magnetic and biological properties from their bulk counterpart due to their high surface to volume ratio. Recently nanofluids have experimentally and theoretically been shown to possess improved acoustical, thermo physical and higher energy efficiency in a variety of systems for different medical and industrial applications, such as cancer treatment, hyperthermia, transportation, military, nuclear energy, in industrial heat recovery, electronic component cooling, lubricants and solar heating systems *etc*.[1]

The study of particle-fluid interaction by non destructive ultrasonic techniques provides valuable information regarding nature and strength of interactions through association, dissociation, agglomerisation, internal structure, internal pressure, free volume, cohesive energy, complex formation *etc*. It also provides the range of concentration of solute at which system becomes more effective. The interactions among liquid molecules arise, due to several causes, such as electrostatic forces, dispersion forces, cohesive forces, van der Waal's forces, donor-acceptor interactions and H-bonding *etc.*

In the present work we have prepared the silver nanoparticle in powder form from silver nitrate of AR grade by thermal decomposition method. As silver is monovalent therefore $AgNO_3$ is taken in crucible then it is grind and mixed at atomic level with 0.8834 gm of urea used as a fuel. Then combustion was took place in furnace at 700°C. The prepared nanoparticles dispersed in methanol under sonication for homogeneous suspension. Attempt has been made to characterize the nanoparticle using an ultrasonic technique. Ultrasonic velocity, density and viscosity measurement have been carried out as a function of concentration of nanoparticles for different temperature of silver nanofluids. The

obtained results are useful to understand the effect of concentration and temperature. This help to realize the mechanism of cluster formation and interactions occurs in the present nanofluids system.[2]

Experimental

Materials and Instruments

High purity and and AR grade silver nitrate (AR 98%), urea from were used. The ultrasonic velocity is measured using ultrasonic interferometer at a standard frequency of 1MHz with an accuracy of ± 0.01m/s. The temperature of sample was maintained constant within ± 0.1°C by circulation of water by thermostatically regulated constant temperature water bath. Density measurement was carried out using specific gravity bottles with accuracy of 0.001mg ?.

Experimental procedure

Preparation of Samples

The silver nanoparticle were synthesized by thermal decomposition method at 700°C. Reducing agent NH_2CONH_2 is added to the mixture of $AgNO_3$ in order to form the silver nanoparticle.

Step I :

$$2AgNO_3 + H_3N - CO\ ?\ NH_3 \rightarrow Ag_2O + NO_2\uparrow + CO_2\uparrow + NH_3\uparrow + 2[H]$$

Step II :

$$Ag_2O + 2[H] \rightarrow 2Ag + H_2O\uparrow$$

Balance the equations. It is NH_2CONH_2

During the thermal heating, silver nitrate and urea molecule under high temperature gets decomposed into silver oxide, nitrogen dioxide, carbon dioxide, ammonia and Nascent hydrogen. Nascent hydrogen is highly reactive and reduce the silver oxide into silver at high temp. 700°C and silver nanoparticles is obtained. All the gaseous produce due to thermal decomposition gets released.

In the preparation of methanol based silver nanofluids two step method have been employed. Nanoparticles used in this method are first produced as a dry powder and the nanosized powder is then dispersed into a fluid in a second processing step. Drzazga et al. prepared metal oxide-water nanofluids by two-step method[3]. This step-by-step method isolates the preparation of the nanofluids from the preparation of nanoparticles.

Results and Discussion

The structure of prepared silver nanoparticles has been investigated by X-ray diffraction (XRD) analysis. XRD pattern of silver nanoparticles is taken and it is compared with standard JCPDS data of silver, it is hold good. Typical XRD pattern of sample, prepared by the present chemical method are shown in the Fig.1.

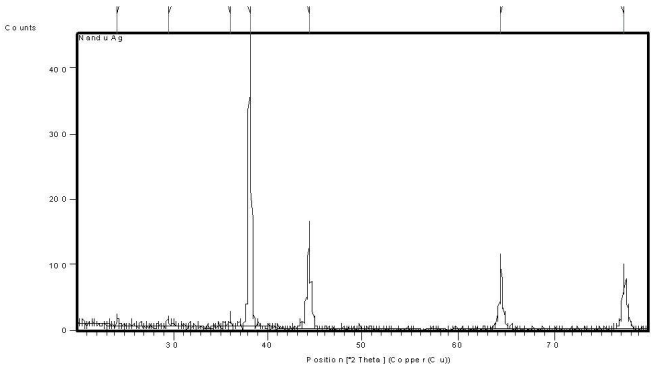

Fig. 1 X-ray diffraction pattern of Ag nanoparticles.

The X-ray diffraction pattern of the silver nanoparticles synthesized by thermal decomposition method is shown in Fig. 1. Miller Indices (h k l) is assigned to each peak in first step. A number of strong Bragg reflections can be seen which correspond to the (111), (200), (220) and (311) reflections of FCC silver. No spurious diffractions due to crystallographic impurities are found. All the reflections correspond to pure silver metal with face centered cubic *(fcc)* symmetry. The high intense peak for *fcc* materials is generally (1 1 1) reflection, which is observed in the sample. The intensity of peaks reflected the high degree of crystallinity of the silver nanoparticles. However, the diffraction peaks are broad indicating that the crystallite size is very small.

The XRD study indicates the formation of silver nanoparticles. Table1 shows the experimentally obtained X-ray diffraction angle and the standard diffraction angle of Ag specimen.

From this study, average particle size has been estimated by using Debye-Scherrer formula

$$D = \frac{0.9\lambda}{W\cos\theta}$$

Where 'λ' is the wavelength of X-ray (0.1541 nm), 'W' is FWHM (full width at half maximum), 'θ' is the diffraction

angle and 'D' is particle diameter (size). The average particle size is found to be around 30 nm.

Ultrasonic Velocity Measurements

As the ultrasonic velocity is highly sensitive to the local structure, molecular interaction and can be used to provide qualitative information about the physical nature and strength of interaction between suspended particles and suspending medium. Ultrasonic velocity is useful in gaining insight into the structure and bonding of associated molecular complexes[4]. we applied it here to examine its value in pure methanol and methanol based silver nanofluids. All the measurements are made at the frequency of 1 MHz. The results of the concentration and temperature dependent ultrasonic velocity are presented in Fig. 2 and Fig. 3 respectively. Ultrasonic waves of frequency 1 MHz are formed by a quartz plate fixed at the bottom of the cell. The waves are altered by a movable metallic plate kept parallel to the quartz plate. If the separation between these plates is exactly a whole multiple of the sound wavelength, standing waves are formed in the medium. The acoustic resonance gives rise to maximum anode current. The distance between the plates is now increased or decreased. Maximum anode current is observed when the variation is half wavelength or multiple of it. From the knowledge of wavelength ? and frequency f the velocity of ultrasonic wave can be obtained by the relation, $V = f . \lambda$

The compressibility can be calculated by the equation,

$\beta = \frac{1}{\rho V^2}$ where, ρ is the density of the fluid.

The variation in ultrasonic propagation shows analogous behavior with increase in concentration of silver nanoparticles in methanol. The ultrasonic velocity slightly decreases with increase of nanoparticles concentration and shows a deep at lower concentrations 0.006M indicating weak interactions between the constituents. But at higher concentration 0.008M there is a sudden increase in velocity followed by slight increment with loading of nanoparticles indicates strong interactions between the constituents. This anomalous behavior of ultrasonic velocity can be interpreted in term of dipole-induced dipole interaction. When silver NPs dispersed into alcoholic medium like methanol, partially negative oxygen atom interact with silver nanoparticles and induced polarization of silver nanoparticles, take place. Hence dipole-induced dipole type of interaction

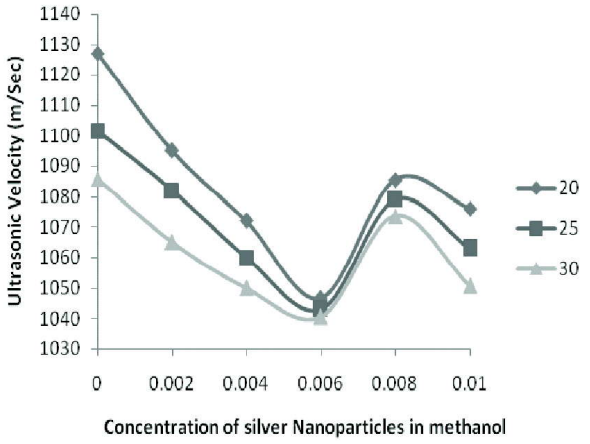

Fig. 2 Variation of Ultrasonic velocity

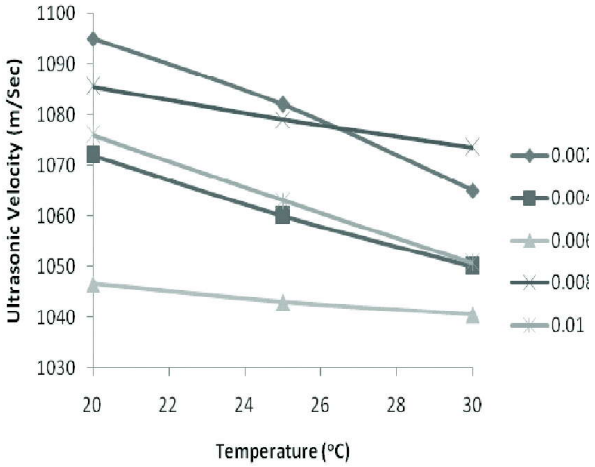

Fig. 3 Temperature dependence ultrasonic velocity in methanol base Ag nanofluids

occurs between the methanol molecule and silver nanoparticles at higher concentration. It is observed that ultrasonic velocity decreases with increase in temperature, this id due to Brownian motion of nanoparticles in methanol based nanosuspension and thermal agitation[5].

The adiabatic compressibility is the fractional decrease of volume per unit increase of pressure, when no heat flows in or out. From Fig. 4 it is clear that compressibility of nanofluid decreases with increase in concentration of nanoparticles in methanol. As expected, the nanofluids studied shows compressibility minima at 0.008 M concentration in the same region of concentration where ultrasonic velocity maxima occur. Decrease in adiabatic compressibility at 0.008 M concentration is attributed to fact that strong cohesive interaction forces act among the molecules and atoms after the dispersion of silver nanoparticles in methanol6. Fig. 5 shows the temperature

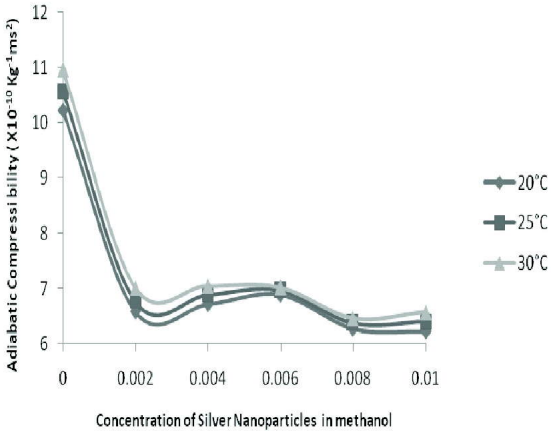

Fig. 4 Variation of adiabatic compressibility

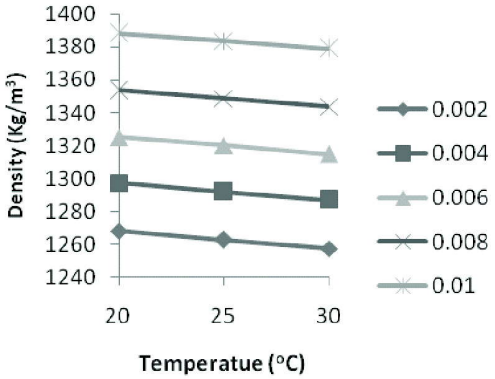

Fig. 5 Temperature dependence density of methanol base Ag nanofluids

dependence density of methanol based silver nanofluids. It is observed that density of silver nanofluids is higher than the base fluid (methanol) and increase with increase in molar concentration of silver nanoparticles in methanol. This indicates the close packing between the constituents in the nano material suspension. As temperature increases, density of dispersion medium (methanol) decreases. Also added nanoparticles and base fluid have a different coefficient of thermal expansion[7]. Hence density of methanol based silver nanofluids decreases with rise in temperature.

Conclusion

The formation of silver nanoparticles by Thermal decomposition method was examined by means of spectroscopic study. From X-ray diffraction analysis using Debay Scherrer formula, the average crystalline size is determined to be 30 nm. Homogeneous suspensions of silver nanoparticles in methanol are prepared with different concentrations using magnetic stirrer. Ultrasonic velocity and density studies were carried out for the prepared nanofluids at a temperature varies from 20°C to 30°C. Interaction between the silver nanoparticles and methanol molecules was analyzed using acoustical parameters. From the analysis, it is evident that the particle-fluid interaction in methanol based nanofluids is effective at 0.008 M concentration shows strong interaction between the particles and methanol. Such particles-fluid interaction studies are helpful to understand the reason behind anomalous variation in acoustical properties between silver nanoparticles and methanol molecules, which arise due to dipole-induced dipole type of interaction, and agglomerisation of nanoparticles is considered the main reason for the ultrasonic velocity enhancement.

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Study of acoustical parameters of dextran in 2 (M) glycine using ultrasonic technique at different frequencies

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The propagation of ultrasonic waves and the measurement of their velocity in solutions form an important tool for evaluation of various acoustical and thermo dynamical parameters which are shown to be useful in understanding the solute-solvent interaction and packing effect of solutes with solvent molecules. The thermo-physical parameters density, ultrasonic velocity and viscosity have been measured for Polymer dextran in 2 (M) glycine at 308 K, at four different frequency *i.e.,* 1 MHz, 5 MHz, 9 MHz and 12 MHz at different concentration of dextran. Using the experimental values of density, viscosity and ultrasonic velocity some of the acoustical parameters likefree volume, internal pressure, absorption coefficient or attenuation coefficient, Rao's constant and Wada's constant have been calculated keepingtemperatureconstant at 308 K. The variation of these parameters with change in concentration and frequency has been discussed in the light of solute-solvent and solute-solute interaction.

Keywords: Aqueous dextran, ultrasonicvelocity, free volume, internalpressure, attenuation coefficient.

Introduction

The practical importance of solution rather than single component liquid systems has gained much importance during the last two decades in assessing the nature of molecular interactions and investigating the physio-chemical behaviour of such systems. The interactions between different molecules are responsible for mixing properties of solvents, and these interactions influence over the value of physico-chemical properties[1-2]. We have studied earlier physical properties of binary mixtures, involving separation units for industrial, food engineering or pharmaceutical applications. In this paper, values of η, ρ, U and related thermodynamic and acoustic parameters have been determined and the solute-solvent interactions for the aqueous solution of dextran of different concentration have been studied with four different frequencies 1 MHz, 5 MHz, 9 MHz &12 MHz at 308 K temperature. Prior to this studies we have taken this sample to study the parameters like acoustic impedance, adiabatic compressibility, intermolecular free length and Gibb's free energy, at different temperature[3].

Dextran, a water soluble polymer, is aα-D-1, 6-glucose linked glucan with side chainsl-3 linked to the backbone units of polymer. Dextran are synthesised from sucrose by certain species of the family such as streptococcus and lactobacillus. Dextran develops naturally in sucrose containing solutions that have been included with dextran producing bacteria from air, plants or soil. It is the only polysaccharide that is water soluble. Dextran and their derivatives find wide applications in various industries particularly in pharmaceutical sector[4,5].The fast increasing of these polyglucosansfor medical[6,7,8], industrial and research[9] purposes motivated to carry out investigation of thermo acoustic parameter of dextran by ultrasonic technique.

Experimental section

Materials

Polymer dextran of molecular weight 70,000 used as solute, is of Analytical Reagent (AR) grade, manufactured by HI Media Laboratories Private Limited,

India. Solvent such as aqueous solution of 2(M) glycine an Analytical Reagent (AR) grade, manufactured by Merck Specialties Private Limited are used as such throughout the experiments.

Methods

Velocity Measurement

The ultrasonic interferometer model is used for measuring velocity have been calibrated by taking some standard liquids like benzene and carbon tetrachloride. The velocity of ultrasonic wave in the solution of dextranin aqueous solution of 2(M) glycine at different concentrations have been measured using multi-frequency ultrasonic interferometer having ±0.1°C degree of accuracy at 1 MHz, 5 MHz, 9 MHz, 12 MHz frequency. The measuring cell consists of a specially designed double walled vessel with provision of maintaining constant temperature at 308K. An electronically operated digital constant temperature bath operating in the temperature range -10°C to 85°C with an accuracy of ± 0.1°C has been used to circulate water through the outer jacket of the double walled measuring cell containing the experimental liquid.

Density Measurement

The densities of the experimental mixture are measured using a 25 ml specific gravity bottle by relative measurement method with an accuracy of ±0.01 kg·m^{-3}. The specific gravity bottle with the experimental mixture was immersed in the temperature-controlled water bath. The weight of the sample was measured using an electronic digital balance and calculated using standard equation mentioned in theory below.

Viscosity measurement

The viscosity of solution is measured using an Oswald's viscometer calibrated with double distilled water. The Oswald's viscometer with the polymer solution is immersed in the temperature controlled water bath. The time of flow was measured using a racer stop watch with an accuracy of 0.01 at above mentioned temperatures and calculated using standard equation.

Theoretical Aspect

The following thermodynamic and acoustic parameters have been calculated:

Free volume (V_f)

Free volume *(V_f)* in terms of ultrasonic velocity (U) and the viscosity (η) of liquid is[10] as follows:

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

Where M_{eff} is the effective molecular weight of the mixture ($M_{eff} = \Sigma m_i X_i$, where m_i and X_i are themolecular weight and mole fraction of individual constituents respectively), K is the temperature independent constant which is equal to 4.281×10^9 [11] for all liquids.

Internal pressure (π_i)

$$\pi = bRT\left(\frac{K\eta}{U}\right)^{3/2}\left(\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right)$$

Where b stands for cubic packing, which is assumed to be 2 for all liquids, k is a dimensionless constant independent of temperature and nature of liquids. Its value is 4.281×10^9. T is the absolute temperature in Kelvin, M_{eff} is the effective molecular weight, R is the universal gas constant, η is the viscosity of solution in Ns·m^{-2}, U is the ultrasonic velocity in m·s^{-1}, and ρ is the density in kg·m^{-3} of solution.

Absorption coefficient or attenuation coefficient

It is a characteristic of the medium. It depends on the external condition like temperature, pressure, and frequency of measurement. It is given by the following relation[12]

$$\alpha = \frac{8\pi^2\eta f^2}{3\rho U^3}$$

Where f is the frequency of ultrasonic wave.

Rao's constant

Rao has established the empirical relation between molecular weight, density and ultrasonic velocity of liquids as

$$R = \frac{M_{eff}}{\rho}U^{1/3}$$

This equation is called Rao's rule and R is also called as the molar sound velocity Rao provided a theoretical explanation of his Rao's formula on the basis of phase rule and kinetic theory of liquids[13].

Wada's constant

Wada had analyzed the variation of molar compressibility with concentration for many liquid systems. He derived the empirical relation[14],

$$W = \frac{M_{eff}}{\rho}\beta^{-1/7}$$

Results and Discussion

The experimental data relating to density, viscosity, andvelocity at 308 *K* for frequencies 1, 5, 9 and 12 MHz for the given mixture have been presented in Table 1 and Table 2. Calculatedvalues of free volume, internal pressure, attenuation coefficient, Rao's constant and Wada's constant are presented in Tables 2-4.

Table 1 – Values of density and viscosity of dextran with (2 M) glycine in different concentrations at 308 K temperature.

T (Kelvin)	Concentration									
	0.10%		0.25%		0.50%		0.75%		1%	
	ρ kg.m^{-3}	η 10^{-3} N.s.m^{-2}	ρ kg.m^{-3}	η 10^{-3} N.s.m^{-2}	ρ kg.m^{-3}	η 10^{-3} N.s.m^{-2}	ρ kg.m^{-3}	η 10^{-3} N.s.m^{-2}	ρ kg.m^{-3}	η 10^{-3} N.s.m^{-2}
308	1051.88	0.96	1053.47	0.99	1054.26	1.02	1055.05	1.09	1055.85	1.12

Table 2 – Values of ultrasonic velocity and freevolume ofdextran with (2M) glycine in different concentrations and frequency at 308 K temperature

	Ultrasonic velocity (U) m/s				Free volume (V_f) (x10^{-3} m^3·mol^{-1})			
Conc.	1 MHz	5 MHz	9 MHz	12 MHz	1 MHz	5 MHz	9 MHz	12 MHz
0.10%	1620.67	1613.00	1609.20	1606.80	7.87	7.82	7.79	7.77
0.25%	1621.33	1614.75	1611.90	1608.60	7.54	7.49	7.47	7.45
0.50%	1622.00	1615.50	1612.35	1611.00	7.13	7.09	7.07	7.06
0.75%	1622.67	1617.75	1615.50	1613.40	6.51	6.48	6.47	6.45
1%	1623.50	1620.00	1616.00	1614.00	6.25	6.23	6.20	6.19

Table 3 – Values of internal pressure and attenuation coefficient of dextran with (2M) glycinein different concentrations and frequency at 308 K temperature

	Internal pressure (× 10^3 N·m^{-2})				Attenuation coefficient (x 10^6 (np·m^{-1})			
Conc.	1 MHz	5 MHz	9 MHz	12 MHz	1 MHz	5 MHz	9 MHz	12 MHz
0.10%	123.60	123.89	124.04	124.13	10.390	262.540	853.556	1528.494
0.25%	125.54	125.79	125.90	126.03	9.120	230.161	749.246	1335.975
0.50%	127.93	128.19	128.32	128.37	8.319	209.673	684.232	1222.314
0.75%	131.96	132.16	132.25	132.34	7.650	192.308	625.075	1113.920
1%	133.84	133.99	134.15	134.24	7.051	177.291	576.297	1025.852

Table 4 – Values of Rao's constantand Wada's constantof dextran with (2M) Glycine at different concentrations and frequency at 308 K temperature

	Rao's constant R (m^3/mole)(m/s)$^{1/3}$(10^{-3})				Wada's constant W (m^3/mole)(N/m^2)$^{1/7}$(10^{-3})			
Conc.	1 MHz	5 MHz	9 MHz	12 MHz	1 MHz	5 MHz	9 MHz	12 MHz
0.10%	1.117	1.115	1.114	1.113	2.122	2.119	2.118	2.117
0.25%	1.115	1.114	1.113	1.112	2.120	2.117	2.116	2.115
0.50%	1.114	1.113	1.112	1.112	2.119	2.116	2.115	2.115
0.75%	1.114	1.113	1.112	1.112	2.118	2.116	2.115	2.114
1%	1.113	1.112	1.111	1.111	2.116	2.115	2.114	2.113

By addition of dextran in glycine the structure of both solute and solvent isdisrupted. Therefore Dextran occupies the interstitial space of glycine and tends to break the original ordered state of glycine. Interaction between solute and solvent molecules results in decrease in free length and increase in density and viscosity with increase of solute concentration.

It is observed that increase of ultrasonic velocity with increase in concentration (vol.%) of dextran in glycine indicates structural readjustment of molecular packing tacking in solution. For a given concentration and temperature, ultrasonic velocity decreases with increase in frequency. Such a decrease in velocity is an indication of weak molecular association between the components of the solute and solvent molecules.

It isobserved that free volume decreases and internal pressure increases withincrease in concentration (vol.%) of dextran in glycine.Thus it shows exactly the opposite trend with concentration to that of internal pressure as expected indicating association in the molecules of the component liquids. The decrease in free volume with increase in concentration suggests that the molecules arrange themselves in such a way that the void space is less available. Therefore it shows decrease of compressibility. At constant concentration of component liquid and constant temperature, viscosity remains constant, hence

$$V_f \alpha\ U^{3/2}$$

Since velocity decreases as frequency increases, hence free volume also decreases.

Internal pressure, the measure of forces of interaction contributes to the overall cohesion or adhesion of the liquid system. When concentration of Dextran increases, internal pressure increases as the force of cohesion increases as in Table 3. The observed increase values of internal pressure in system aredue to close association between solute and solvent molecules.Since the association of the interacting molecules varies with the frequency of the ultrasonic wave, the cohesive force between the molecules also varies. Cohesive force as well as internal pressure increase slowly as frequency increases.

Absorption coefficient, which is a characteristic of the medium, increases with increase in frequency. As frequency increases, absorption coefficient increases rapidly as it is proportional to the square of the frequency. This shows a similar behavior to that of the passage of electromagnetic waves through a conductor where the skin depth decreases with frequency of the incoming wave. Decrease in skin depth means increase in absorption. As concentration increases, absorption coefficient decreases gradually, at low frequency (1 MHz) the absorption coefficient is negligible and more effective if we increase the frequency. The decrease in absorption coefficient with increase in concentration suggests that the molecules arrange themselves in such a way that the void space is less available showing decrease of free volume.

To study the existence of molecular interactions Rao's constant and Wada's constant are alsoan important. It is observed that Rao's constant and Wada's constant decrease with the increase of concentration and frequency as shown in Table 4. This indicates close packing of solute and solvent molecules indicating interaction .

Conclusion

The different acoustic parameters are studied for different concentration of Dextran in 2 M glycine, by changing the frequency while keeping the temperature constant. When the frequency increases, the molecules move rapidly and have little time to interact. Hence the change in the acoustic parameters is negligible. However, the changes are more prominent in some of the other parameters. Increase of viscosity and internal pressure with concentration shows strongersolute solvent interaction in the solution. The free volume, Wada's constant and Rao's constant decrease with rise in concentration. This shows that solute solvent interaction in the system takes place and supports the facts shown by variation of internal pressure. The results show that the specific solute-solvent interactions are explained from the thermo acoustic parameters. However, any deviation from the usual behavior is probably due to characteristic structural changes in the respective system.

The thermodynamic as well as acoustic parameter suggest a molecular association existing in the solution. Also the addition of solute into the solvent brings about further stronger interaction between solute-solvent in the solution.

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Excess thermo acoustical parameters of binary mixture ammonium hydroxide and ethanol

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The ultrasonic velocity (U) density (ρ) and viscosity (η) of binary liquid mixture of Ammonium Hydroxide with ethanol have been measured over the entire range of compositions at the temperature 313K and frequency 1MHz. The observed basic experimental data have been utilized to evaluate some of the derived thermo acoustic parameters such as free volume, internal pressure, relaxation time and Gibbs free energy. The behavior of these parameters and the excess values of free volume, Internal pressure, relaxation time, and Gibbs free energy were evaluated with composition of the mixture and have been discussed in terms of nature and strength of molecular interactions between the constituents.

Keywords: Ultrasonic velocity; acoustical parameters; molecular interactions.

Introduction

The ultrasonic study of inter molecular interactions plays an important role in the development of molecular sciences. In the recent years, ultrasonic technique has become more powerful tool in providing information regarding the behavior of liquids and solids owing to its ability of characterizing physiochemical behavior of the medium[1-3]. Ultrasonic velocity measurements are useful in the field of interactions and structural aspect studies, for characterizing the Physico-chemical behavior of liquid mixtures[4-7]. Ultrasonic measurements of acoustic parameters with change in mole fraction give an insight in to the molecular process[8-10]. This type of study has increased in recent years due to industrial applications. Many researchers have undertaken these studies qualitatively through ultrasonic velocity, density adiabatic compressibility and viscosity measurements[11-15]. NH_4OH is ingredient of cleaning agent. It is toxic, corrosive in nature It is used in industry, to darken or stain wood containing tannic acid.Used.in food production, as acidity regulator. Aqueous ammonia is used in qualitative inorganic analysis, as a complexant and base. Ethanol (CH_3CH_2OH) is used as a solvent, used in the manufacture of varnishes & perfumes, used as preservative for biological specimen, used in explosives, automotive fuel industry, drug applications. It is volatile, flammable and colorless. Ammonium Hydroxide and aliphatic alcohol Ethanol are versatile fluids and has been used on a wide range of fields and applications, hence chosen.

In view of extensive applications of ammonium hydroxide and ethanol in the engineering process, pharmaceutical industries, present study provides qualitative information regarding the nature and strength of molecular interactions in the liquid mixture of ammonium hydroxide+ ethanol at the temperature 313K through the derived parameters from ultrasonic velocity, density and viscosity measurements. The present investigation is undertaken, in order to study the dependence of the relative strength of intermolecular interaction and their nature in pure liquids and liquid mixtures. The results are discussed in terms of molecular interactions.

Theoretical aspect

From basic experimental data of U, ρ and η, various acoustical parameters such as (τ), (ΔG), (π_i), (V_f) and their Excess Parameters τ^E, ΔG^E, π_i^E and V_f^E are calculated.

Relaxation time (τ)

Relaxation time (τ) is the time taken for the excitation energy to appear as translational energy and it depends on temperature and on impurities. The dispersion of ultrasonic velocity in binary mixture reveals information about the characteristic time of the relaxation process that causes dispersion Relaxation time (τ) can be calculated as :

$$\tau = (4/3)\ \beta_{a*}\ \eta \qquad (1)$$

Gibb's free energy (ΔG)

The relaxation time for a given transition is related to the activation energy. The variation of relaxation time (τ) with temperature (T) can be expressed in the form of eyring self process theory.

$$1/\tau = [(k_B T)/h]*\exp(-\Delta G/k_B T) \qquad (2)$$

The above equation can be rearranged as,

$$\Delta G = (-k_B T)\log[h/(k_B T\tau)] \qquad (3)$$

or

$$\Delta G = (k_B T)\log[(k_B T\tau)/h] \qquad (4)$$

Where k_B is the Boltzmann's constant (1.3806×10^{-23} JK^{-1}), h is the plank's constant ($h = 6.63\times10^{-34}$ Js), T is the absolute temperature and τ is the relaxation time.

Internal pressure (π_i)

$$\tau_i = (b\ RT)[(K * \eta)/(U)]^{1/2}* [(\rho^{2/3})/(M_{eff}^{7/6})] \qquad (5)$$

Where, b is the cubic packing which is assumed to be 2 for all liquids and solutions, K is the temperature independent constant 4.28×10^9 for all liquids. T is the absolute temperature, R is universal gas constant, η be the viscosity and M_{eff} is the effective molecular weight.

Free Volume (V_f)

$$V_f = [(M_{eff}\ U)/(K\ \eta)]^{3/2} \qquad (6)$$

Where, M_{eff} (Effective mass) = $\Sigma\, m_i\, x_i$, in which m_i and x_i are the molecular weight and the mole fraction of the individual constituents respectively. K is the temperature independent constant, which is equal to $4.28 * 10^9$ for all liquids and η be the coefficient of viscosity[16-17].

Excess parameters (A^E)

Excess parameter represents the difference between the parameters of real mixtures $(A_{exp.})$ and those corresponding to an ideal mixture $(A_{id.})$

$$A^E = A_{exp.} - A_{id} \qquad (7)$$

Where $A_{id.} = \Sigma A_i X_i$, $i = 1, 2, 3, n$. A_i is any acoustical parameters and x_i the mole fraction of the liquid components. T is the absolute temperature = 313 K., M is the molecular weight, X is weight fraction, After calculations, graphs were plotted for excess parameters vs mole fraction (X) of ammonium hydroxide (NH_4OH) in ethanol (CH_3CH_2OH) for 313 K and f = 1 MHz.

Experimental Details

The liquids were of analar grade and redistilled before use. The binary liquid mixture of different mole fractions of the two components, namely ammonium hydroxide and ethanol were prepared immediately before use at 1 MHz and 313 K, Velocity of Ultrasonic wave (U) and density (ρ) in the mixtures were measured by ultrasonic multi frequency interferometer and using pycknometer by relative measurement method with an accuracy of ± 0.1 kgm^{-3}. The Digital thermostat maintains the temperature constant of the samples, by circulating water through double walled measuring cell, made up of steel containing experimental solution of different molarities at the desired temperature. An Ostwald's viscometer (calibrated) was used for viscosity (η) measurement of pure liquids and liquid mixtures with accuracy of ±0.001 Ns/m^2. The setup is checked for standard liquids. All the necessary precautions were taken to minimize the possible experimental error. The present work was conducted under normal pressure.

The variations of τ^E, ΔG^E, π_i^E and V_f^E w.r. to mole fraction (X) of the system: Ammonium Hydroxide + Ethanol at T = 313K and 1 MHz frequency are given in Table 1.

Results and Discussion

Experimental density (ρ), viscosity (η) and ultrasonic velocity (U) values and the derived parameters such as relaxation time (τ), Gibb's free energy (ΔG), internal pressure (π_i) and free Volume (V_f) for the binary system

Table 1 – Density *(ρ)*, Velocity *(U)*, viscosity *(η)*, relaxation time *(τ)* & Gibb's free energy *(ΔG)* Internal pressure (π_i), and Free Volume (V_f) and Excess parameters such as τ^E, G^E, π_i^E and V_f^E of Ammonium Hydroxide + Ethanol at *T*= 313 K and at 1 MHz frequency, in MKS system are shown.

Mole fraction (x)	ρ kg/m^3	U (m/s)	$\eta*10^{-3}$ (cp)	$\tau*10^{-12}$ (S.)	$\Delta G*10^{-20}$ kj mole^{-1}
0	822.70	1130.00	0.7520	0.9803	0.3480
0.1	824.21	1210.00	0.6350	0.7618	0.3006
0.5	845.45	1601.33	0.3200	0.2389	0.0830
1	915.00	2410.00	0.1170	0.0597	-0.1770
π_i*10^6 (Pa.s)	V_f*10^{-7} m^{3}mol^{-1}	τ^E*10^{-12} (s.)	ΔG^E*10^{-20} kJ mole^{-1}	$\pi_i^E*10^6$ (Pa.S)	$V_f^E*10^{-7}$ m^{3}mole^{-1}
0.2796	2.0571	0.0000	0.0000	0.0000	0.0000
0.2557	2.8326	-0.1264	0.0052	-0.0071	-5.9438
0.1810	10.3252	-0.2811	-0.0025	-0.0145	-25.3290
0.1116	69.2512	0.0000	0.0000	0.0000	0.0000

ammonium hydroxide and ethanol at frequency 1 MHz and temperature 313 K are given in the Table 1. The variation of excess relaxation time, excess Gibb's free energy, excess internal pressure and excess Free Volume versus mole fraction *(X)* of ammonium hydroxide and ethanol at temperature 313 K and frequency 1 MHz are shown in the Table 1.

Excess relaxation time (τ^E) decreases below zero with increasing the mole concentration of the solute in system, becomes minimum and then increases. The dispersion of the ultrasonic velocity in the system may contain information about the characteristics time *(τ)* of the relaxation process that causes dispersion. The relaxation time which is in the order of 10-12 second is due to structural relaxation process[18] and in such a situation, it is suggested that, the molecules get rearranged due to co-operative process[19-20]. It represents the presence of weak interaction between the solute and solvent molecules. From Table 1 it is observed that all parameters show nonlinear behavior which suggests some interactions between the constituents.

Excess Gibb's free energy (ΔG^E) remains constant very near to zero then decreases with increasing mole fraction of the solute in the systems and again increases. This may be due to the intermediate complex compound formation between the binary liquids, due to molecular dissociation. It is observed that, generally the decrease in Gibb's free energy favors the formation of product from reaction. This observation confirms the formation of hydrogen bonding in the binary mixture (see fig. 2).

Table 1 contains the excess internal pressure (π_i^E) and excess free volume (V_f^E) versus mole concentration *(x)*. It is observed that excess internal pressure and excess free volume decreases below zero, becomes minimum and then increases with increase in molar concentration of ammonium hydroxide in ethanol indicating increase in dipole association in the molecules of the components. Such behaviour of excess internal pressure and excess free volume generally indicates the association through hydrogen bonding. This suggests the close packing of the molecules inside the shield.

Conclusion

Molecular interactions exist between the solute and the solvent in the binary liquid mixtures of ammonium hydroxide and ethanol.

Sometimes higher degree of molecular interactions also exists between constituent molecules of ammonium hydroxide and ethanol in the binary liquid mixtures.

Weak dispersive type intermolecular interactions are confirmed in the binary liquid mixtures.

The nonlinear behavior of excess thermo acoustic parameters provides the knowledge about various interactions among the molecules.

Excess parameters (positive or negative) help to compare experimental values with ideal (standard) values, which lead to better understanding of the system under consideration.

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Ultrasonic studies of Cu (II) soaps derived from groundnut and seasame oils

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Ultrasonic speed have been measured in pure and binary mixtures containing copper soaps derived from groundnut and sesame oils in 20 % and 40% methanol benzene mixture. From these values, the specific acoustic impedance, adiabatic compressibility, intermolecular free length, apparent molar compressibility, molar sound velocity, primary solvation number have been calculated. The results have been fitted to Masson equation. The results have been explained on the basis of intermolecular interactions.

Keywords: Copper soaps, methanol, groundnut oil, sesame oil, ultrasonic speed.

Introduction

The ultrasonic studies are extensively used to estimate the thermodynamic properties and to predict the intermolecular interactions of binary mixtures[1]. Ultrasonic investigation of liquid mixture have significant importance in understanding intermolecular interaction between the component molecules as that finds application in several industrial and technological processes[2]. Derived parameters from ultrasonic velocity measurements provide qualitative information regarding the nature and strength of molecular interactions in liquid mixtures[3]. This has been studied for various binary and ternary mixtures with respect to variation in concentration of the liquids and temperatures[4]. A number of workers have discussed the physico-chemical aspects of ultrasonic velocity and related parameters on different types of soaps and detergents[5]. 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 mixture[6]. Ultrasonic measurements have also been used to determine solvation number in aqueous media.

Methodology

Copper soap was prepared by refluxing the oils with ethyl alcohol and 2 N KOH solutions for 3-4 hours (Direct Metathesis). The neutralization of excess of KOH present was done by slow addition of 0.5N HCl. Saturated solution of copper sulphate was then added to it, for conversion of neutralized potassium soap into their corresponding copper soaps. Copper soap so obtained was then washed with warm water and 10% alcohol at 50°C and recrystallized using hot benzene. Molecular weights of Copper soaps were determined from saponification values7. The copper soap are abbreviated as copper - groundnut (CG) and copper -sesame (CSe).The ultrasonic velocity was determined with the help of a single crystal ultrasonic interferometer model M-82 working at a fixed frequency of 2 MHz. Water was maintained at 30°C and controlled up to +0.1°C by a thermostat was passed through the jacket of the cell before the measurement was actually made. The measured velocities have an uncertainty of 0.5 ms^{-1}. Further the operative part of the measurement involves the slow movement of micrometer till the anode current meter shows a maximum. A number of maxima readings of anode current are passed on and their number 'n' is counted. The total distance *(d)* thus moved by the micrometer gives the value of wavelength *(λ)* with the help of the following relation:

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

Once the wavelength is known, the velocity *(u)* in the liquid can be calculated with the help of the following relation:

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

Acoustic Parameters

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 by using the following relationships[8] :

$$Z = u.\rho \quad (3)$$

$$\beta_{ad} = 1/u^2\rho \quad (4)$$

$$L_f = K\sqrt{\beta_{ad}} \quad (5)$$

$$\varphi_k = [1000.(\beta\rho_0 - \beta_0\rho)/c\rho_0] + \beta_0 M/\rho_0 \quad (6)$$

$$R = M.(u)^{1/3}/\rho \quad (7)$$

$$M = X_1M_1 + X_2M_2 + X_3M_3 \quad (8)$$

$$S_n = [n_0/n].[1 - V\beta/n_0V_0\beta_0] \quad (9)$$

Where β_0, β, $\rho_0.\rho$, n_0, n, V_0, V are adiabatic compressibility, density, numbers of moles and molar volume of solvent and solute respectively. *K, c* and *u* are the temperature dependent Jacobson's constant, having value 6.31×10^4 concentration in g mol l^{-1} and ultrasonic velocity. The expression for molar volume of solvent, V_0 and soap solution V may be written as under :

$$V = \frac{X_1M_1 + X_2M_2 + X_3M_3}{\rho} \quad (10)$$

$$V_0 = \frac{X_1M_1 + X_2M_2 + X_3M_3}{\rho_0} \quad (11)$$

In equation (6), (8) and (9), *'M'* represent the molecular weight and *'X'*, the mole fraction of the component. Here the subscript 1, 2 and 3 refer to soap, methanol and benzene respectively.

Results and Discussion

The following thermodynamic and acoustic parameters have been calculated :

(1) *Copper soap derived from groundnut and seasam oils in 20% methanol-benzene mixture*

Acoustic Parameters : The experimental values of *'u'* and allied parameters for the above referred systems are recorded in (Tables 1-2). The data clearly indicate that the values of *u, Z*, 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 value 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 waves.

The decrease in intermolecular free length *'L_f'* with increase in soap concentration indicates that there is

Table 1 – Ultrasonic velocity and other acoustic parameters of copper soap derived from groundnut oil in 20% methanol-benzene mixture (CG_{20}).

c (mol l^{-1})	ρ (g dm^{-3})	u × 10^{-5} (m s^{-1})	Z × 10^{-5} (g cm^{-2} s^{-1})	β_{ad} × 10^{11} (cm^2 $dyne^{-1}$)	L_f × 10^{10} (A^0)	$-\varphi_k$ × 10^8	R × 10^{-2}	S_n × 10^{-3}
0.0003	0.8588	1.4898	1.2794	5.2466	0.4571	-425.1	38.17	-90.740
0.0004	0.8590	1.5152	1.3015	5.0710	0.4493	122.1	38.38	-64.609
0.0006	0.8595	1.5705	1.3498	4.7173	0.4334	674.6	38.82	-38.440
0.0008	0.8599	1.6400	1.4103	4.3237	0.4149	999.9	39.37	-24.974
0.0010	0.8601	1.7101	1.4708	3.9757	0.3979	1148.0	39.92	-17.262
0.0011	0.8599	1.7406	1.4967	3.8384	0.3909	1167.2	40.17	-14.726
0.0012	0.8600	1.7707	1.5228	3.7086	0.3843	1178.4	40.40	-12.652
0.0013	0.8603	1.8018	1.5501	3.5804	0.3776	1187.4	40.62	-10.903
0.0014	0.8606	1.8349	1.5791	3.4514	0.3707	1195.8	40.86	-9.399
0.0016	0.8610	1.8868	1.6245	3.2625	0.3604	1165.4	41.23	-7.298
0.0018	0.8615	1.9417	1.6728	3.0786	0.3501	1139.2	41.60	-5.684
0.0020	0.8620	2.0000	1.7240	2.9002	0.3398	1115.6	42.00	-4.415

Table 2 – Ultrasonic velocity and other acoustic parameters of copper soap (CSe_{20}) derived from seasame oil in 20% methanol-benzene mixture.

c (mol l^{-1})	ρ (g dm^{-3})	u × 10^{-5} (cm s^{-1})	Z × 10^{-5} (g cm^{-2} s^{-1})	β_{ad} × 10^{11} (cm^2 $dyne^{-1}$)	L_f × 10^{10} (A^0)	$-\phi_k$ × 10^8	R × 10^{-2}	S_n × 10^{-3}
0.0003	0.8589	1.4545	1.2493	5.5030	0.4681	-1277.9	37.859	-97.403
0.0004	0.8593	1.4815	1.2730	5.3023	0.4595	-451.5	38.076	-69.090
0.0006	0.8600	1.5504	1.3333	4.8375	0.4389	479.3	38.631	-39.968
0.0008	0.8608	1.6129	1.3884	4.4656	0.4217	829.3	39.112	-26.313
0.0010	0.8616	1.6807	1.4480	4.1091	0.4045	1023.8	39.623	-18.246
0.0011	0.8620	1.7391	1.4991	3.8357	0.3908	1181.0	40.061	-14.640
0.0012	0.8624	1.7544	1.5129	3.7675	0.3873	1141.1	40.162	-12.968
0.0013	0.8624	1.7825	1.5373	3.6494	0.3812	1144.1	40.377	-11.263
0.0014	0.8625	1.8182	1.5682	3.5072	0.3737	1164.0	40.642	-9.667
0.0016	0.8627	1.8779	1.6201	3.2868	0.3618	1156.5	41.079	-7.385
0.0018	0.8630	1.9324	1.6676	3.1032	0.3515	1130.6	41.463	-5.767
0.0020	0.8635	1.9900	1.7184	2.9242	0.3412	1108.2	41.853	-4.489

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 another fact that as the concentration of solute increases, a large portion of solvent molecules are electostricted and the amount of bulk solvent decreases causing the compressibility to decrease. In the present study, dβ/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 Das *et al.*[8] 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[9-10].

Micellar Features : The plots of *u, Z,* β_{ad} and L_f vs *c* are all characterized by an intersection of two straight lines at a definite concentration (Figs. 1-4) corresponding to the CMC of these soap. At CMC, the hydrocarbon chain structure of soap molecules allow extensive contact between adjacent chain, possibly

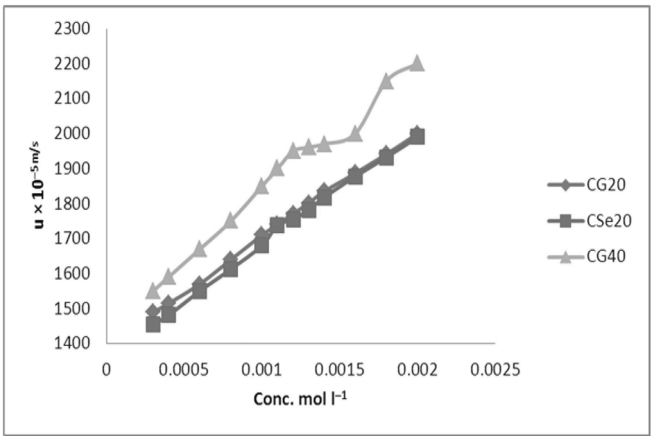

Fig. 1 Plots of *u* versus *c* of copper soaps derived from groundnut and sesame oil in 20% and 40% methanol - benzene mixture

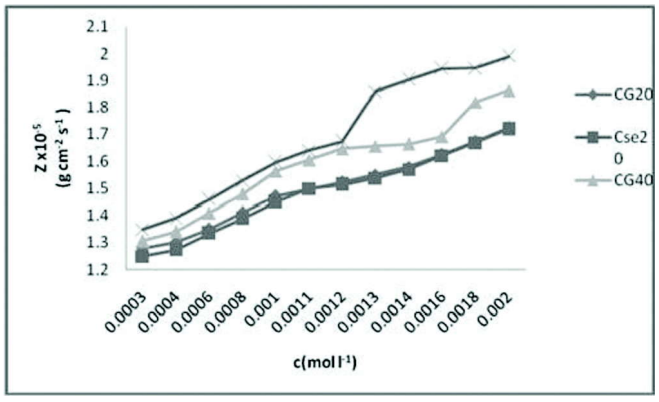

Fig. 2 Plots of *z* versus *c* of copper soaps derived from groundnut and sesame oil in 20% and 40% methanol-benzene mixture

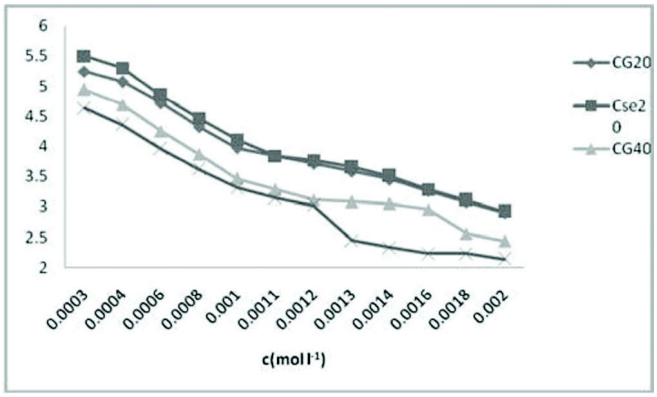

Fig. 3 Plots of β_{ad} versus c of copper soaps derived from groundnut and sesame oil in 20% and 40% methanol - benzene mixture

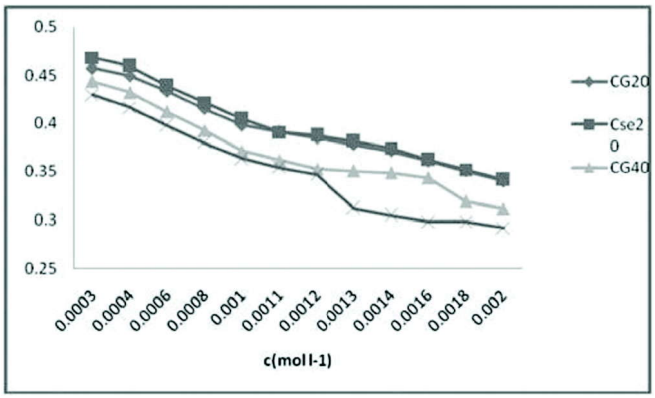

Fig. 4 Plots of L_f versus c of copper soaps derived from groundnut and sesame oil in 20% and 40% methanol-benzene mixture

accompanied by change in vibrational and rotational degree of freedom of methylene group of fatty acids of varying composition present in edible oils. The values of CMC of these soaps are recorded in (Table-5). It is clear that CMC is dependent on the composition of the solvent mixture and composition of the oil (Table-7-8) follows the order:

$$CSe > CG$$

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

The decrease in adiabatic compressibility '?' and intermolecular free length $'L_f'$ of the soap with increasing concentration may be interpreted on the basis of the fact that the ions in solution are enveloped by a layer of solvent molecules firmly bound and oriented towards ions. The orientation of the solvent molecules around the ions (solutes) may be due to the influence of electrostatic fields of ions and results in the increase in the internal pressure and in lowering the compressibility of the solution i.e. the solution becomes harder to compress. This indicates that there is sufficient soap-solvent interaction due to which micellar alignment is considerably affected.

The variation in the extent of decrement of the parameters referred in the preceding parameter suggests that the predomination of benzene (higher percentage of non-polar solvent) play a significant role in compacting the molecular organization of the micelles.

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

$$u = u_0 + Gc \qquad (10)$$

Here $'u_0'$ is the ultrasonic velocity in the solvent. Here $'G'$ is Gruneisen parameter. The value of G is obtained from the slope of the linear plots of $'u$ v/s c' below CMC. The plots of ultrasonic velocity v/s soap concentration (Fig. 1) 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 CMC.

It is interesting to point out that values of the parameters u, Z, β_{ad} and L_f with respect to copper soaps in 20% methanol-benzene mixture follows the order:

$$[u] : CG > CSe$$

$$[Z] : CG > CSe$$

Where as β_{ad} and L_f follows the reverse order *i.e.*

$$[\beta_{ad}] : CG < CSe$$

$$[L_f] : CG < CSe$$

It has been observed that the values of apparent molar compressibility $'\varphi_k'$ decreases sharply up to the CMC followed by curvature and after CMC it increases in all the copper soap derived from various edible oils in 20% methanol-benzene mixture.

The data has also been analyzed in terms of Masson equation[11]. As $'\varphi_k'$ is the function of concentration its value is found to be in good agreement with that obtained from the following equation:

$$\varphi_k = \varphi^0{}_k + S_k\sqrt{c}$$

Where $'\varphi^0{}_k'$ is the limiting apparent molar compressibility and is a measure of solute-solvent interactions. $'S_k'$ is the experimental slope, a measure of

solute-solute interactions. The plot of 'φ_k v/s $\sqrt{c}$ ' is characterized by an intersection of two straight lines followed by curvature in *CG* while for *CSe* it is interaction of two straight line (Fig. 5). In view of two intersecting straight lines for 'φ_k v/s $\sqrt{c}$' plots, it is reasonable to determine two values of both φ^0_k and S_k *i.e.* below and above *CMC*, and are designated as $\varphi^0 k_1$, φ^0_{k2} and S_{k1}, S_{k2}. A perusal of (Table-6) reveals that value of φ^0_{k1} is positive for *CG* and *CSe* where φ^0_{k2} is negative for all the copper soap. The order of the two parameters are observed to be as follows :

$$\varphi^0_{k1} > \varphi^0_{k2} \quad \text{and} \quad S_{K2} > S_{k1}$$

Literature survey reveals that negative values of 'φ^0_k' indicate electrostriction and hydrophobic interaction. The negative values of 'φ^0_k' are also attributed to the loss of structural compressibility of solvent due to strong electrostrictive forces in the vicinity of polar molecules[12]. The change in the values of φ^0_k and S_k below and above *CMC* suggests that there is a phenomenal change in the micellar agglomeration.

(2) *Copper soaps derived from groundnut and seasame oils in 40% methanol-benzene mixture*

Acoustic Parameters : After perusal of the observed data, it may be mentioned that the acoustic parameters and the equations related to ultrasonic investigations for the above referred system having the same trend as has been calculated for 20% methanol-benzene mixture.

Table 3 – Ultrasonic velocity and other acoustic parameters of copper soap derived from groundnut oil in 40% methanol-benzene mixture (CG_{40}).

c (mol l^{-1})	ρ (g dm^{-3})	u × 10^{-5} (cm s^{-1})	Z × 10^{-5} (g cm^{-2} s^{-1})	β_{ad} × 10^{11} (cm^2 $dyne^{-1}$)	L_f × 10^{10} (A^0)	$-\phi_k$ × 10^8	R × 10^{-2}	S_n × 10^{-3}
0.0003	0.8423	1.5504	1.3059	4.9392	0.4435	-334.7	32.396	-81.351
0.0004	0.8427	1.5905	1.3403	4.6912	0.4322	373.7	32.660	-55.850
0.0006	0.8434	1.6701	1.4086	4.2507	0.4114	988.8	33.174	-31.126
0.0008	0.8440	1.7505	1.4775	3.8664	0.3924	1225.3	33.679	-19.356
0.0010	0.8444	1.8501	1.5623	3.4597	0.3711	1388.6	34.294	-12.118
0.0011	0.8440	1.9002	1.6037	3.2815	0.3615	1421.6	34.622	-9.695
0.0012	0.8437	1.9503	1.6454	3.1162	0.3522	1439.4	34.936	-7.758
0.0013	0.8441	1.9608	1.6551	3.0814	0.3503	1356.9	34.985	-6.932
0.0014	0.8444	1.9704	1.6638	3.0502	0.3485	1283.2	35.032	-6.248
0.0016	0.8451	2.0000	1.6902	2.9582	0.3432	1182.3	35.183	-4.982
0.0018	0.8458	2.1505	1.8189	2.5565	0.3190	1276.0	36.019	-2.580
0.0020	0.8464	2.2002	1.8623	2.4406	0.3117	1207.7	36.274	-1.839

Table 4 – Ultrasonic velocity and other acoustic parameters of copper soap derived from seasame oil in 40% methanol-benzene mixture (CSe_{40}).

c (mol l^{-1})	ρ (g dm^{-3})	u × 10^{-5} (cm s^{-1})	Z × 10^{-5} (g cm^{-2} s^{-1})	β_{ad} × 10^{11} (cm^2 $dyne^{-1}$)	L_f × 10^{10} (A^0)	$-\phi_k$ × 10^8	R × 10^{-2}	S_n × 10^{-3}
0.0003	0.8424	1.6000	1.3478	4.6370	0.4297	674.3	32.734	-73.011
0.0004	0.8426	1.6502	1.3904	4.3584	0.4166	1204.4	33.067	-48.985
0.0006	0.8432	1.7301	1.4588	3.9621	0.3972	1467.9	33.574	-27.167
0.0008	0.8438	1.8108	1.5279	3.6144	0.3794	1539.0	34.068	-16.764
0.0010	0.8445	1.8904	1.5964	3.3137	0.3632	1535.1	34.537	-10.911
0.0011	0.8448	1.9408	1.6396	3.1425	0.3537	1552.4	34.831	-8.629
0.0012	0.8450	1.9802	1.6733	3.0180	0.3467	1527.4	35.060	-7.051
0.0013	0.8452	2.2002	1.8597	2.4440	0.3119	1899.1	36.305	-2.936
0.0014	0.8454	2.2510	1.9030	2.3345	0.3049	1798.6	36.578	-2.013
0.0016	0.8457	2.3002	1.9453	2.2349	0.2983	1636.6	36.834	-1.246
0.0018	0.8460	2.3002	1.9459	2.2341	0.2983	1455.7	36.827	-1.102
0.0020	0.8463	2.3502	1.9890	2.1393	0.2919	1358.1	37.084	-0.599

The values of *'u'* and allied parameters for the above referred system are given in (Tables 3-4). It is also observed from the data that the numerical values of *'u'*, *'Z'* and *'R'* increases where- as the values of *'β'* and *'L_f'* decreases with increasing soap concentration. The decrease in the value of *'β'* and *'L_f'* with increasing ultrasonic velocity *'u'* indicates that there is a significant interaction between soap and solvent molecules suggesting a consistent change in the clear micellar orientation in the system[13-14].

Micellar features : The plots of acoustic parameters *i.e.* '*u* v/s *c*', '*Z* v/s *c*', '*β* v/s *c*' and 'L_f v/s *c*' all are characterized by an interaction of two straight lines at a definite soap concentration (Figs. 1-4) corresponding to the *CMC* of the soap. It is obvious from that the *CMC* is dependent on the composition of the solvent mixture. A variation of ultrasonic velocity with soap concentration is equally applicable to these soaps. The values of *G* and u_0 are evaluated from the '*u* v/s *c*' plots. Values of *'G'* for soap solution increases from 20% to 40% methanol-benzene mixture. This obviously suggests that behavior of soap in methanol dominated solvent and benzene dominated solvent is quite different as they occupy different position in the micelles[15-16].

With regard to solvent mixture, the value of *'u'* and *'Z'* increases with the predominance of methanol (in 40% methanol-benzene mixture) where as decreases with the predominance of benzene (in 20% methanol-benzene mixture) in the system under reference (Figs. 1-4). The results are vice-versa for *'β'* and *'L_f'* and follow the order:

$$u : CG > CSe$$
$$\beta : CG < CSe$$

Table 5 – CMC values of copper soaps derived from groundnut and seasame oils in 20% and 40% methanol-benzene.

Plot	CG_{20}	CSe_{20}	CG_{40}	CSe_{40}
u vs *c*	0.00110	0.0012	0.00120	0.0014
Z vs *c*	0.00110	0.0012	0.00120	0.0014
β_{ad} vs *c*	0.00106	0.0012	0.00120	0.0014
L_f vs *c*	0.00109	0.0012	0.00106	0.0014
ϕ_k vs $\sqrt{c}$	0.00110	0.0012	0.00120	0.0014

Table 6 – Values of various constants obtained from masson's equation for copper soaps derived from groundnut and seasame oil sin 20% methanol-benzene mixture.

Name of the soap	$u_0 \times 10^{-5}$	$G \times 10^{-5}$	$\phi^0_{k1} \times 10^8$	$\phi^0_{k2} \times 10^8$	$S_{k1} \times 10^8$	$S_{k2} \times 10^8$
CG_{20}	1.365	0.6494	+9.5	-12.2	-1.0355	0.0694
CSe_{20}	1.355	0.6494	+10.5	-12.1	-1.7320	0.0874
CG_{40}	1.415	0.8390	9.21	-20.3	-1.150	0.4452
CSe_{40}	1.475	0.7812	17.5	--35.7	-0.4877	1.2348

Table 7 – Fatty acid composition of oils used for copper soap synthesis.

Name of oil	% Fatty Acids					
	16:0	18:0	18:1	18:2	18:3	Other Acids
Groundnut Oil	10	4	61	18	—	C_{20}-C_{24} 7%
Sesame Oil	8	4	45	41	—	—

Table 8 – Analytical and physical data of copper (II) soaps derived from groundnut and seasame oils.

Name of Copper Soap	Colour	Melting point (in °C)	Yield %	Metal %		S.V.	S.E.	Average Mol. Wt.
				Found	Calculated			
CG	Green	97	75	9.58	9.60	188.70	297.29	656.08
CSe	Green	100	85	10.05	9.81	191.70	292.64	646.78

This may be attributed to the fact that entrapping of solvent molecules in the palisade layer of micelles at 20% methanol is dissimilar to the entrapping of solvent above this concentration suggesting a consistent change in the micellar behavior with the predominance of benzene and methanol respectively[17-18].

The perusal of data shows (Table-5) that the value of *CMC* of ultrasonic parameter is higher in 40% methanol-benzene as compared to 20% methanol-benzene mixture. With regard to chain length of the soap segment of the molecule, the *CMC* value follows the order:

$$CSe > CG$$

The results are in agreement with the fact that there is decrease in the CMC with the increase in number of carbon atoms in the hydrophobic chain[19-20].

Again the value of apparent molar compressibility $'\varphi_k'$ decreases sharply up to the *CMC* and after *CMC* it increases in all the Copper soap derived from various edible oils in the referred system.

The plots of $'\varphi_k \sqrt{c}$ are characterized by an intersection of two straight line at point corresponds to the *CMC* of the soap (Fig. 5). The values of the parameters below and above *CMC* ?0k1, φ^0_{k1}, φ^0_{k2} and S_{K1}, S_{k2} are evaluated from the intercepts and slops of these plots are recorded in (Table-6).

A perusal of (Table-6) reveals that φ^0_{k1} and φ^0_{k2} values are negative for all these Copper soaps which are indicative of electrostriction and hydrophobic interaction. For all the soap, these parameters are found to be in the given order :

$$\varphi^0_{k1} > \varphi^0_{k2} \quad \text{and} \quad S_{K1} < S_{k2}$$

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Short communications

Thermal conductivity of liquid – interrelationship between thermal conductivity and ultrasonic speed

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A correlation between thermal conductivity (λ) and ultrasonic velocity (u) of liquid has been made. Using the density (ρ) and ultrasonic velocity data for liquids Ar and Kr, the values of λ have been calculated at different temperatures. It is interesting to note that the excellent agreement between experimental and theoretical values is found for both the liquids.

Keywords: Ultrasonic velocity, thermal conductivity, density

Introduction

Thermal conductivity of liquid is one of very important and useful property of liquid. Exhaustive work has been done on the theoretical aspects of thermal conductivity of gases and mixtures of gases. Comparatively less amount of work has been done on thermal conductivity of liquids. One of the most widely employed method for estimating thermal conductivity is to treat liquid as a modified gas, thus gaseous molecule has been extended to study liquid thermal conductivity[1-2]. Some of empirical and semi-empirical approaches[3]. were also employed. A critical review of the estimation of liquid thermal conductivity has been given by Reid, Prausnitz and Poling[4]. During recent past[6-8] above relations were employed to compute thermal conductivities of liquids N_2, Kr and Ar in the light of Flory's statistical theory. In these papers, indirectly sound velocity, has been obtained from Flory theory. This value of u were then, substituted in eq (2) for calculating thermal conductivity, λ, of liquids. In fact it is an indirect approach for the computation of λ from sound velocity, u.

Hirschfeld *et al.*[5] proposed the first correlation between sound velocity (u) and thermal conductivity (λ) as :

$$V = \frac{M}{\rho} \tag{1}$$

where $\gamma = C_p/C_v$, n = number of molecules and k the Boltzmann constant. This equation is for monoatomic liquids. For polyatomic liquids, the equation can be written as :

$$\lambda = 2.80 k n^{2/3} \gamma^{-1/3} u \tag{2}$$

In the present work a direct correlation between sound velocity and thermal conductivity has been made.

Correlation between ultrasonic speed and thermal conductivity

In Eq. (2),

$$n = \frac{N}{V} = \frac{6.02 \times 10^{23}}{V}$$

$$k = \frac{R}{N} = 1.38 \times 10^{-16} \, ergmol^{-1} K^{-1}$$

Substituting the values of k and n we have

$$\lambda = \frac{2.755 \times \gamma^{-13} u}{V^{2/3}} \tag{3}$$

where u is in cms^{-1}, V the molar volume

During recent past[9-12] we have obtained the expression for γ, the heat capacity ratio, in terms of density and ultrasonic speed on the basis of dimensional analysis. The derived expression is

Table 1 – Calculated values of thermal conductivity of liquid Ar

T (K)	ρ (g cm^{-3})	u (ms^{-1})	λ (calcm^{-1}s^{-1}k^{-1})	λ (exp)	Dev. [%]
146.20	1.0620	560.00	1.70	1.70	-0.12
110.90	1.2800	742.00	2.50	2.51	0.27
86.70	1.4020	861.00	3.01	3.00	-0.20
				APD	**1.85**

Table 2 – Calculated values of thermal conductivity of liquid Kr.

T (K)	ρ (g cm^{-3})	u (ms^{-1})	λ (calcm^{-1}s^{-1}k^{-1})	λ (exp)	Dev. [%]
120.00	2.4130	683.00	10.04	9.54	-5.23
150.00	2.1640	554.70	7.74	7.27	-6.50
180.00	1.8470	397.50	5.04	5.41	6.85
180.00	1.8590	406.00	5.17	5.50	5.94
195.00	1.7200	361.20	4.38	4.87	9.98
				APD	**1.82**

$$\gamma = \frac{1.71}{T^{4/9}\rho^{1/3}} \tag{4}$$

Putting the value of γ from eq (4) into eq (3) and simplifying, we get

$$\lambda = \frac{16.21\times10^{-3}uT^{4/27}\rho^{7/9}}{M^{2/3}} \tag{5}$$

where, $V = \frac{M}{\rho}$, M is the molar mass. In eq (5), u, ρ and M are in ms^{-1}, g cm^{-3} and g respectively. Eq (5) is an empirical equation for calculating the value of thermal conductivity (λ) of liquid from the experimental values of ρ and u at temperature T.

Results and Discussion

The validity of eq (5) has been tested by computing the thermal conductivity of liquid *Ar* and *Kr*. The experimental data of ultrasonic velocity *(u)* and density (ρ) were taken from different sources[7-12]. The experimental values of λ and its computed values for Ar are recorded in Table 1. Whereas, the same computed values of λ for liquid *Kr* are shown in Table 2. It appears from the results of Table 1 and Table 2 that the agreement between theoretical and experimental λ values are excellent for both the liquids *Ar* and *Kr*.

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Ph.D Thesis Summary

Anomalies of ultrasonic velocities and elastic properties in $R_{1-X}A_XMnO_3$ perovskite manganite materials

(Awarded 2016 by Manonmaniam Sundaranar University, Tirunelveli, Tamil Nadu to Dr. M. Arunachalam, Sri S.RamasamyNaidu Memorial College, Sattur, Tamil Nadu)

In this research work, the scholar prepared mixed valent perovskite materials with the general formula $La_{1-X}A_XMnO_3$ (A-calcium, sodium and gadolinium) with different values of *x* using solid state reaction technique. He explored the structural and morphological characteristics such as crystal structure, crystalline size and size of particles of the prepared samples employing studies such as x-ray diffraction (XRD)and scanning electron microscope (SEM). He confirmed the elemental composition of the prepared perovskite samples with the obtained energy dispersive x-ray spectrometrypatterns.

He carried out *in-situ* measurements of various ultrasonic parameters such as longitudinal velocity, shear velocity, longitudinal attenuation and shear attenuation over a wide range of temperature. The measured ultrasonic parameters were used to evaluate the elastic constants of the samples and to explore the phase/structural transition in the prepared perovskite samples. The anomalous behaviour shown by these materials on the temperature dependent ultrasonic parameters yield much information on the characteristics of these materials.

He obtained the ferromagnetic (FM) to paramagnetic (PM) transition temperature T_C for the samples $La_{1-x}Na_xMnO_3$. The values of T_C are 320, 328 and 334 K for the *x* values 0.10, 0.15 and 0.20 respectively. It is seen from the observation that T_C increases with the increase of sodium content in the sample. This behaviour is ascribed to the increase in double exchange (DE) interaction caused by the reduction in Mn-O distances that takes place because of doping. It is due to the increase in average ionic radius of La site produced by the substitution of sodium. It is to be noted that the ionic radius of La^{3+} is 1.36A° and that the Na^{1+} is 1.39 A°. Further, as the concentration of sodium increases, the decrease in Mn-O distances and the increase in Mn-O-Mn bond cause a reduction in $Mn^{3+}O_6$ octahedralJahn-Teller distortion. This in turn leads to an increase in T_C. As the value of T_C is around the room temperature, the monovalent sodium doped perovskite manganite is suitable for potential applications. Further, from the similarity in the behaviour in the temperature dependence of longitudinal and shear attenuation, it is observed that the prepared perovskite materials reveal linear magnetostriction effect rather than volume magnetostriction.

In-situ ultrasonic measurements on the prepared $La_{1-x}Ca_xMnO_3$ perovskite material samples with *x* = 0.70, 0.75 and 0.90 over a wide range of temperature facilitate him to derive precise information on the metal-insulator transition that took place in the samples. The study on calcium mixed $LaMnO_3$ yielded the Metal-insulator transition temperature (T_{MI}) values as 640, 570 and 370 K for the corresponding *x* values of 0.70, 0.75 and 0.90. From these values, it is evident that the T_{MI} shifted towards lower temperature as the composition of calcium increases. This is attributed to the fact due to the increase in substitution of Ca, the distortion of $Mn^{3+}O_6$ octahedron due to Jahn-Teller effect comes in to play. From the area of the anomalous region, one could predict the level of magnetic entropy that the material possesses. In his examination, the areas of anomalous region in the case of U_L are 85,132.5 and 210 m s^{-1} K for the *x* values of 0.90, 0.75 and 0.70 respectively. It is evident that area becomes wider as the content of calciumdecreases.The obtained wider area is associated with the effect of large disorder which confirms the increase in magnetic entropy with the decrease in calcium content in the samples.

The investigation carried out on $La_{1-x}Gd_xCrO_3$ (*x* = 0.10, 0.15 and 0.20) samples, subjecting them to *in-situ* ultrasonic measurements over a wide range of temperatures from 300 to 700 K reveals the temperature dependent structural phase transition in these perovskite material. Literature survey confirmed that the structural transition was from orthorhombic to rhombohedral. The structural transition temperature (T_S) is 484, 456 and 422 K respectively for the different doping levels *x* = 0.10, 0.15 and 0.20 in the material.

Besides these, he attempted to tune the metal-insulator transition temperature (T_{MI}) in LCMO materials. In this investigation he prepared pellets of $La_{0.3}Ca_{0.7}MnO_3$ perovskite materials sintered at different temperatures such as 900, 1000, 1100 and 1200°C for 24 h. The samples are coded as LCMO900, LCMO1000, LCMO1100 and LCMO1200 respectively. The structural, and morphological studied were carried out from the obtained XRD patterns and SEM images. The EDX spectra of the prepared LCMO perovskite samples confirmed the elemental composition of them. The temperature dependent measurement of the ultrasonic parameters revealed that the metal-insulator transition temperature T_{MI} for the samples LCMO900, LCMO1000 are 635 and 630 K respectively and it is 640 K for both LCMO1100 and LCMO1200 samples. Further, it is noted that T_{MI} of $La_{0.3}Ca_{0.7}MnO_3$ perovskite materials increases with an increase in sintering temperature.

Thus, the research work made effective use of the ultrasonic study, a vital non-destructive evaluation technique.

Journal of Pure and Applied Ultrasonics

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INFORMATION FOR AUTHORS

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