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Molecular interactions in $CdCl_2/H_2C_2O_4$ nanofluid using acoustical studies at room temperature

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Nanofluids have been prepared by dispersing nanometer size particles in base fluid. The very essence of nanofluids research and development has to enhance the fluid macroscopic and mega scale properties such as thermal conductivity through manipulating microscopic physics. The acoustical properties of rhombohedral symmetry $CdCl_2/H_2C_2O_4$ nanofluids have been studied using ultrasonic technique at room temperature (303 K). The ultrasonic velocity, density and viscosity of nanofluids have been measured to manipulate the acoustical parameters such as specific acoustic impedance, adiabatic compressibility, internal pressure, viscous relaxation time, relative association, Gibbs free energy, intermolecular free length to know the molecular interaction. The particle size of $CdCl_2/H_2C_2O_4$ fluid was estimated by using UV-Vis analysis. The results were discussed and compared with experimental and theoretical facts.

Keywords: $CdCl_2/H_2C_2O_4$, Nanofluid, Molecular interactions

1 Introduction

By using ultrasonic technique, the detection and characterization of the microstructure as well as flaw in materials are possible. Controlling materials behaviour based on physical mechanism, the future performance of the materials has been studied. In ultrasonic characterization, the wave propagation velocity is the key parameter and provides the information about crystallographic texture. The ultrasonic velocity is directly related to the elastic constants by the relationship $V=(C/\rho)^{1/2}$, where C is the relevant elastic constants and ρ is the density of that particular material. The elastic constant of a solid gives the valuable insight into the nature of atomic bonding forces and also related with hardness[1]. The ultrasonic waves have many advantages in comparison to other imaging modalities, which leads to its widespread use in clinical practices. It is harmless due to operation at low power and cost effective. Matsu o *et al*[2]. reported the experimental investigation on elastic behaviour and phase stability in *hcp* structure of Ag-Zn alloys using an ultrasonic pulse echo overlapping method. Nanofluids is the composition of fluid suspensions with nanometer-sized particles, which have thermal conductivities far superior to that of the liquid alone. In the light of above scientific importance, it has many applications in various fields including energy, bio and pharmaceutical industry and chemical, electronic, environmental, material, medical and thermal engineering[3]. Nanofluids have at least four relevant scales i.e. the molecular scale, microscale, macroscale and megascale. The molecular scale is characterized by the mean free path between molecular collisions, the microscale by the smallest scale at which the law of continuum mechanics apply, the macroscale by the smallest scale at which a set of averaged properties of concern can be defined and the megascale by the length scale corresponding to the domain of interest[4].

In the present paper, $CdCl_2/H_2C_2O_4$ nanofluids were prepared by varying the molar concentration of $CdCl_2$ in oxalic acid ($H_2C_2O_4$). The acoustical properties have been studied by using the ultrasonic technique at fixed frequency at room temperature (303 K).

2 Experimental Details

All the chemicals used in the present study were of AR grade (S D Fine, India), which was used without further purification. Purity of sample at the time of measurement was 99%. The nanofluids $CdCl_2/H_2C_2O_4$ were prepared by varying molar concentration (0.01-0.05 M) of $CdCl_2$ in base liquid oxalic acid. The CdC_2O_4 (cadmium oxalate) was formed as per the scheme 1.

$$CdCl_2 + H_2C_2O_4 \rightarrow CdC_2O_4 + 2HCl \quad \ldots(1)$$

The ultrasonic velocity in nanofluids was measured using an ultrasonic interferometer (Mittal Make, India) at fixed frequency (2 MHz) with an uncertainty

of ± 0.005% at room temperature 303 K. The mixtures of different compositions were prepared by mass measurement using digital balance with an uncertainty of 10^{-6} Kg. The uncertainty in the density values measurements is ±0.0001 g cm^{-3}. The viscosity was measured with uncertainty ±0.003 mPa s. The measuring cell was a specially designed double walled vessel with provision for temperature constancy. The high frequency generator excites a quartz crystal fixed at the bottom of the measuring cell at its resonant frequency. The density of nanofluids was measured using specific gravity bottle. The viscosity was measured using an Ostwald's viscometer calibrated with doubly distilled water. The UV-VIS spectra of 0.3 M $CdCl_2/H_2C_2O_4$ were recorded by adjusting baseline with $H_2C_2O_4$ on Perkin Elmer UV-VIS spectrometer.

3 Results and Discussion

The values of ultrasonic velocities, density and viscosity are listed in Table 1 at room temperature (303 K). The values of ultrasonic velocities, density and viscosity increase with an increase in molar concentration of $CdCl_2$ in base liquid oxalic acid.

3.1 UV-VIS Analysis

The UV-Vis analysis was carried out to know the optical band gap of 0.3 M $CdCl_2$/ $H_2C_2O_4$ nanofluid. The UV-Vis spectrum is shown in Fig. 1.

The particle size depends on optical band gap. By considering absorption edge at 360 nm of $CdCl_2$, average particle size was estimated by using the hyperbolic band model[5] as in Eq. 2.

$$R = \sqrt{\frac{2\pi^2 h^2 R_{bulk}}{m^*(E_{nano}^2 - E_{bulk}^2)}} \quad \ldots(2)$$

where R is quantum dot radius ($2R$ is the diameter and hence the average particle size) E_{bulk} is bulk band gap[6] (2.52 eV), E_{nano} is band gap of nanomaterial (3.35 eV), m^* is effective mass of electron (m^*=29.15×10^{-31} Kg). The average particle size was found to be 7.84 nm.

Table1 — Values of ultrasonic velocities, density and viscosity measured at room temperature (303 K)

Concentration (M)	Ultrasonic velocity (m/s)	Density (Kg/m^{-3})	Viscosity (Nsm^{-2}) × 10^{-3}
0.01	1120	947	0.670
0.02	1400	947.9	0.675
0.03	1520	948.22	0.685
0.04	1760	949.97	0.726
0.05	2040	953.3	0.758

3.2 Specific Acoustic Impedance

The reflection of ultrasonic waves is due to the acoustic impedance, mismatch at the interface of two media. This is the principal physical property, which allows studying the molecular interaction. The specific acoustic impedance is given as in Eq. 3.

$$Z = u \times \rho \quad \ldots(3)$$

where u and ρ are ultrasonic velocity and density of nanofluids, respectively. The acoustic impedance was found to increase with increase of density in all the five molar concentrations as shown in Fig. 2. This

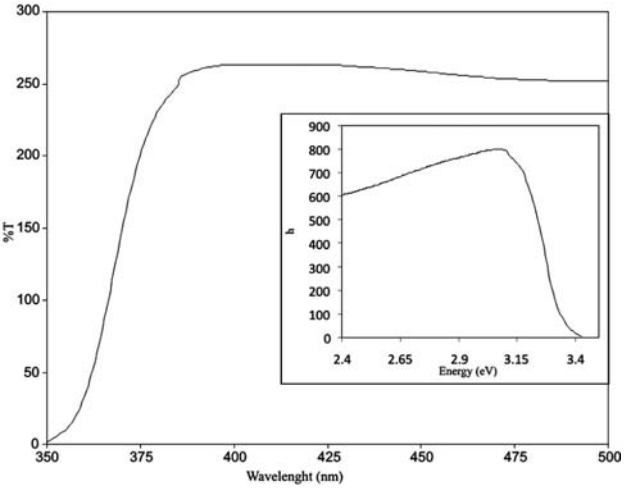

Fig. 1 — UV-VIS spectra of 0.03 M $CdCl_2$/ $H_2C_2O_4$ nanofluid. Inset shows the plot between energy and $\alpha h\nu$

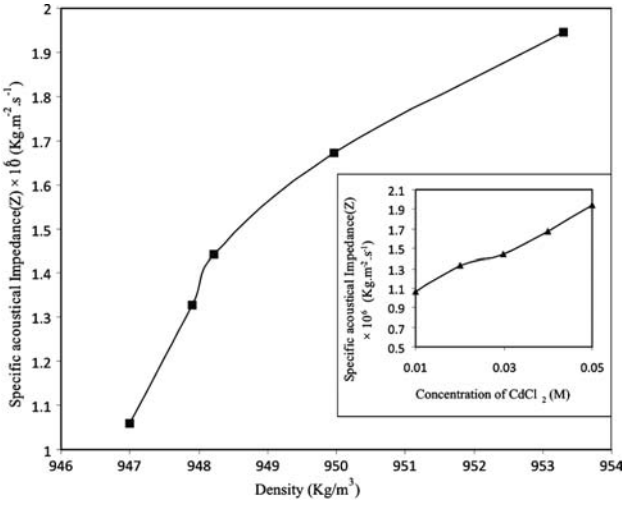

Fig. 2 — Specific acoustical impedance increases with increasing density that represents CdC_2O_4 acquired the fluid properties

represents esteemed interaction between $CdCl_2$ and $H_2C_2O_4$. The linearity in specific acoustic impedance with density shows that the CdC_2O_4 acquired the fluid properties.

The specific acoustical impedance is the confrontation to travel the sound wave encounter as it passes through a medium. The dependence of ultrasonic velocity on density leads to the acoustic impedance. As the density of system increases, so does acoustic impedance. Therefore, acoustic impedance is directly proportional to the density, which is found to be very well agreement with present investigation.

3.3 Adiabatic Compressibility of Solution (βs)

The adiabatic compressibility is the fractional decrease of volume per unit increase of pressure, when no heat flows in or out. It can also be calculated from the ultrasonic velocity (u) and the density of the medium (ρ) using Newton Laplace equation[7] (Eq. 4).

$$\beta_s = 1/u^2\rho \quad \cdots(4)$$

The adiabatic compressibility was found to decrease with increasing density, which results in increase of ultrasonic velocity, as shown in Fig. 3. Theoretical estimation of adiabatic compressibility in mixtures offers simple and convenient way to study the molecular interaction. This shows good agreement with the theoretical analysis[8].

The decrease in compressibility implies that there is an enhanced molecular interaction in this system with increased solute content. The formed new entities become compact and less compressible due to molecular association. This shows an added support for the structure intensifying property of the $CdCl_2$ as well as the presence of appreciable dipole-dipole interaction between $CdCl_2$ and $H_2C_2O_4$ molecules. As a result, solutes may gain mobility and have more probability of contacting solvent molecules, which lead to enhance the interaction between solute and solvent molecules. The decreased adiabatic compressibility represents the pronounced clusterization of the $H_2C_2O_4$ molecules around the positive ions in the solution[9]. The ions Cd^{2+} may come from ionisation of salt molecules in the system.

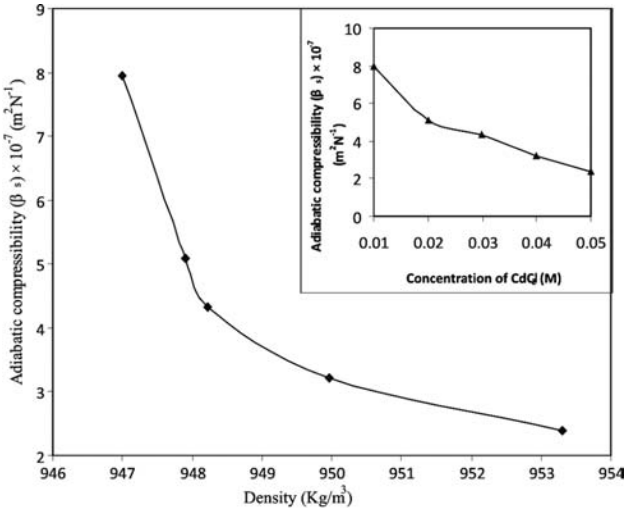

Fig. 3 — Adiabatic compressibility decreases with increasing density that implies there is an enhanced molecular association in nanofluids

3.4 Internal Pressure (π_i)

The internal pressure is the cohesive force, which is resultant of force of attraction and force of repulsion between the molecules [10]. It also gives an idea of the solubility characteristics. The internal pressure was found to increase with density. This shows increase in ultrasonic velocity (Fig. 4.). Thus, the solubility characteristic between $CdCl_2$ and $H_2C_2O_4$ is proportional up to 0.05 M concentration. Internal pressure is estimated using the relation[11]:

$$\pi i = bRT(K\eta/u)^{1/2}\rho^{2/3}/M_{\text{eff}}$$

where $M_{\text{eff}} = x_1M_1 + x_2M_2$. b is constant, K is temperature dependent constant and R is gas constant. The internal pressure describes the physical interaction contribution to the cohesive energy

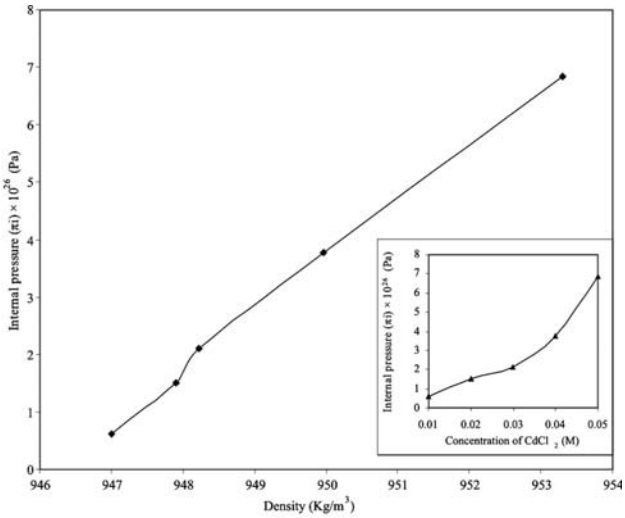

Fig. 4 — Internal pressure increases linearly with increasing density that shows solubility proportional up to 0.05 M

density, which is a measure of the total molecular cohesion per unit volume[12]. It also gives an idea about the solubility characteristics. In finding, the internal pressure increases slowly with increase in molar concentration of $CdCl_2$.

3.5 Viscous Relaxation Time (*t*)

Relaxation time is the time taken for the excitation energy to appear as transnational energy and it depends on temperature and impurities. The relaxation time (*t*) can be calculated from the Eq. 5.

$$t = 4\eta/(3\rho u^2) \quad \ldots(5)$$

The relaxation time found to decrease with increasing molar concentration as shown in Fig. 5. This similar change is found in viscosity. This shows that the viscous forces play a dominant role in the relaxation process. The ultrasonic attenuation of the solutions may decrease with increasing concentration, shows a similar trend to that of acoustical relaxation time. This may be due to a modification in the nature of the molecular interaction.

3.6 Relative Association (R_A)

Relative association is influenced by two factors breaking up of associated solvent molecules on addition of solute and the salvation of solute[13] is shown as in Eq. 6.

$$R_A = (\rho/\rho_0)*(u_0/u)^{1/3} \quad \ldots(6)$$

where ρ_0 is the density of solvent (distilled water =995.65 kg/m^3), u_0 the ultrasonic velocity of distilled water =1460 m/s. In the present study, the relative association was found to decrease with increase in density (Fig. 6).

3.7 Gibbs Free Energy (ΔG^*)

The relaxation time is related to the activation free energy. It can be estimated using Eq. 7.

$$\Delta G^* = -KT \log[h/KTt] \quad \ldots(7)$$

where *K* is Boltzman costant, *T* the temperature, *t* the relaxation time and *h* is Planck constant. The Gibb's free energy was found to decrease with increase in mole fraction of $CdCl_2$ (In present study, the relative association was found to decrease with increase in density (Figs 6 and 7). This leads to the formation of an intermediate compound[14] between $CdCl_2$ and $H_2C_2O_4$.

3.8 Intermolecular Free Length (L_f)

The adiabatic compressibility of nanofluids can be expressed in term of the intermolecular free length. The distance between the surfaces of the neighbouring molecules i.e. intermolecular free length was observe to decrease with increase in molar concentration of $CdCl_2$ with density (Fig. 8).

It is a predominant factor in determining the variation of ultrasonic velocity in fluids. It has been observed that, intermolecular free length decreases with increase in $CdCl_2$ concentration up to 0.04 M. Further, it increased gradually at room temperature.

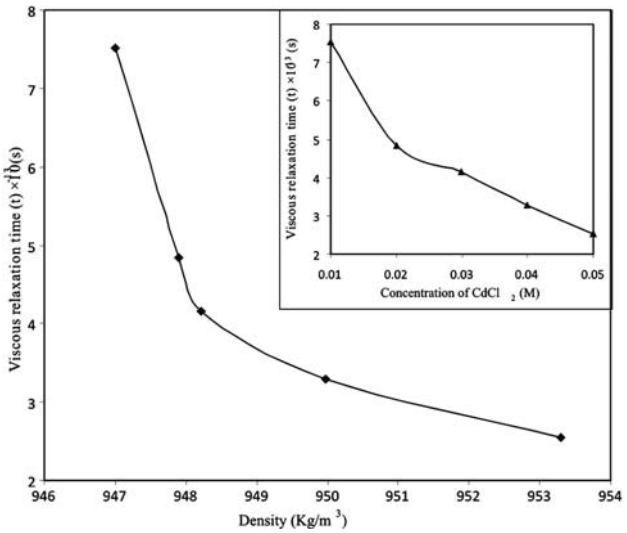

Fig. 5 — Relaxation time decreases with increasing density, which represents ultrasonic attenuation in nanofluids

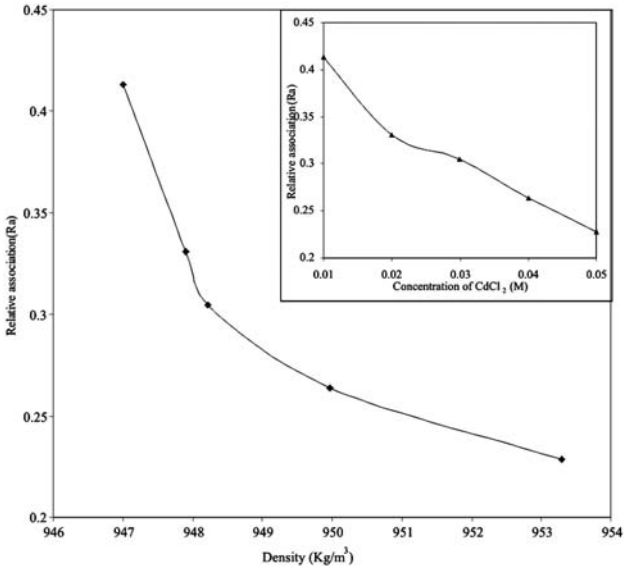

Fig. 6 — Relative association found to decrease with increasing in density

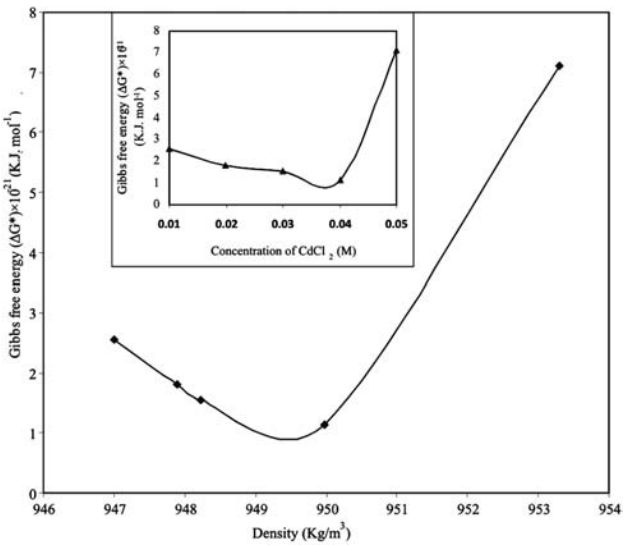

Fig. 7 — Gibb's free energy decreases with increasing density that shows the formation of an intermediate compound between $CdCl_2$ and $H_2C_2O_4$

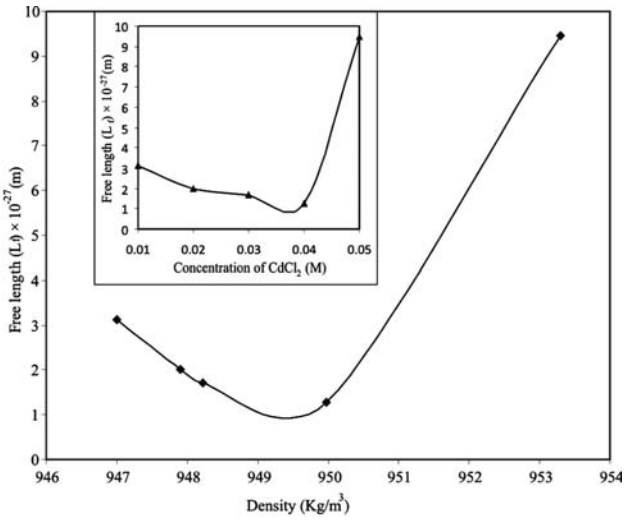

Fig. 8 — Intermolecular free length decreases with increasing density. This result agrees with adiabatic compressibility

Intermolecular free length is computed using the relation[15], $L_f=K(\beta_s)^{1/2}$, where K is temperature dependent Jacobson constant and β_s is adiabatic compressibility. The variation of intermolecular free length (L_f) with concentration is shown in Fig. 8.

4 Conclusions

The ultrasonic technique is an easy technique to analyse acoustical properties of nanofluids. The particle size of nanoparticles dispersed in 0.3 M $CdCl_2/H_2C_2O_4$ nanofluid was found to be 7.84 nm estimated using UV-Vis analysis. The specific acoustic impedance and internal pressure of nanofluids were found to increase with increase in density and molar concentration of $CdCl_2$. The internal pressure shows solubility characteristics between $CdCl_2$ and $H_2C_2O_4$ which are proportional up to 0.05 M concentration. The adiabatic compressibility, viscous relaxation time and relative association were found to decrease with increase in density. Consequently, the Gibbs's Free energy also decreases. This shows the intermediate compound formation between $CdCl_2$ and $H_2C_2O_4$ i.e. CdC_2O_4. The intermolecular free length leads to the presence of specific molecular interaction between the molecules in the nanofluids, which decreases up to 0.04 M concentration after that increases rapidly.

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