Ultrasonic Characterization of Silver Nano Fluid

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Abstract. Nano fluids are stable suspensions of nano particles in a liquid. Metal oxide nanoparticles offer great merits over controlling rheological, thermal, chemical and physical properties of solutions. The effectiveness of a nanoparticle to modify the properties of a fluid depends on its diffusive properties with respect to the fluid. An important application of Nano fluids containing nano particles is as a coolant, since the addition of only a few volume percent of nano particles to a liquid coolant and significantly improves its thermal conductivity. A heat exchange device using nanofluid needs to operate at best nanoparticle loading to get the maximum heat transfer performance. Due to its antimicrobial properties, the future therapeutic directions may include nano-silver as an anti-inflammatory and as anti-platelet agents and antiviral drugs. Owing to the applications of nano silver particles, attempts has been made in the present study to synthesis silver nano particles and characterized with the help of ultrasonic technique. Different acoustic properties of AgNO₃ nanofluids are studied with the help of Ultrasonic technique. Silver nanofluids are synthesized by chemical reduction method. The chemical reduction method involves the reduction of AgNO₃ in aqueous solution by a reducing agent in the presence of a suitable stabilizer, which is necessary in protecting the growth of silver particles from aggregation. Ultrasonic velocity and density values are measured for different concentrations of AgNO₃ nanofluids. The acoustic parameters like adiabatic compressibility, intermolecular free length, and acoustic impedance are calculated from the experimental data. The variation of ultrasonic velocity and other parameters with particle concentration are discussed on the basis of interaction of ultrasonic wave with the nano sized silver particles.

Keywords: Nanofluid, silver nanofluid, ultrasonic velocity, acoustic parameter

1. Introduction

Nano science has blossomed its demand and dominancy from the last decade and the need for nanotechnology will increase as miniaturization becomes more and more essential in areas such as computing, sensors and biomedical applications. Nanofluids are novel suspensions of nano solid particle in base liquids. When a very small amount of guest nano particles, dispersed uniformly and suspended stably in base liquid, they provide dramatic improvements in the physico - chemical and thermal properties of base liquid [1]. One fascinating feature of nano fluids is that they have anomalously high
thermal conductivity [2-3], which make nano fluids strong material for the next generation of coolants for improving the design and performance of thermal management systems. The Brownian motion of nano particles in base liquid is proposed to be one of the major physical mechanisms of the thermal conduction of nano fluids [4-6]. Therefore; it is significant to investigate the movements of nano particles in nano fluids. Ultrasonication is an accepted technique for study of such Brownian motion and dispersing aggregated nanoparticles for the preparation of aqueous nano suspensions. Most of the studies [7] have focused on the effect of sonication time on the stability of nanofluids and all of them used continuous ultrasonic waves to sonication. The ultrasonic property of solid–liquid suspensions in micrometer size of particles causes a change in ultrasonic velocity and ultrasonic attenuation which affects the thermal conductivity of the nanofluids [8]. More recently there has been an increasing interest in the acoustical properties of suspensions for acoustic telemetry through drilling fluids as well as arising demand for ultrasonic particle size instrumentation. Several scientists have made the study of ultrasonic propagation behavior through the suspension of solid particles particularly in micrometer or millimeter size in a liquid aiming to identify the mechanism that enable useful information to be extracted from the behavior of ultrasonic properties, such as particle size, concentration and mechanical properties of the constituents. Because of their high surface to volume ratio, nanoparticles suspended in base liquid, significantly revealing some new properties which are not present in either of the pure materials. Therefore, the investigation of the influence of nanoparticles on the properties of a base liquid is necessary in order to be able to better predict the final properties of the complex fluids. In the present work we have made the study of the propagation of ultrasonic wave in a colloidal solution with dispersed Ag-metal nanoparticles .We prepared stable nanofluids containing silver metal nanoparticles suspended in the base fluid like water. Even though reports are available on the thermal conductivity and viscosity of nanofluid, very little work is reported on the acoustical parameters of nanofluid. Hence, an attempt is made in this work to prepare nanofluid of Ag and study their acoustical parameters. Ag nanofluid is prepared using one step chemical method with water as base fluid. Ultrasonic velocity measurements are carried out on Ag nanofluid and the results are discussed in detail.

2. Material and chemicals

Silver nitrate (AgNO₃, 99.9%), tannic acid (C₇₆H₅₂O₄₆, Mᵦ = 1701), K₂CO₃ were all purchased from Sigma-Aldrich and used without further treatment. All of the solutions were freshly made for the synthesis of silver nanoparticles, especially the freshly made tannic acid aqueous solution, which was ice bathed before use. All solutions were prepared using distilled water.

The present work, describes a green protocol using tannic acid, a polyphenolic plant extract, as both the reducing and stabilizing agent. Tannic acid has been studied extensively for its antioxidant properties and as a chelating agent for several inorganic cations. The representative structure of tannic acid, corresponding to its average formula weight, is shown in Fig.1. It consists of a central core of glucose that is linked by ester bonds to polygalloyl ester chains. Tannic acid at its natural acidic pH is known to be a weak reducing agent that can only grow seeds into nanoparticles at room temperature.
Tannic acid has a pH value between seven and eight, depending on its extent of dissociation and is known to partially hydrolyse under mild acidic/basic conditions into glucose and gallic acid units. Gallic acid at alkaline pH reduces silver nitrate into silver nanoparticles rapidly at room temperature, but the particles form aggregates in solution as gallic acid is a poor stabilizing agent. Glucose is a weak reducing agent at room temperature, but it is a good stabilizing agent at alkaline pH. These findings suggest that tannic acid could be an ideal reducing and stabilizing agent under alkaline conditions at room temperature.

3. Synthesis of silver nanoparticles

One-step chemical method is followed for synthesis of metallic nanoparticles, since the nanoparticles are dispersed in the base fluid as they are produced. This process helps in preventing oxidation of the particles and minimized the agglomeration of nanoparticle. Silver nano fluid was prepared by chemical reduction method using tannic acid as a reducing agent. 35mg of tannic acid was weighed and dissolved in 150 ml of water in a beaker. From this solution 20 ml was further diluted with 40 ml of distilled water which gives total 60 ml solution. After this 30 mg of K₂CO₃ powder was weighed and added to this 60 ml solution due to which there is slight change in colour i.e. pale yellow colour appeared and it was covered with a parafilm. Then 0.22g of AgNO₃ was exactly taken and transferred to 100ml volumetric flask to get 0.00132M standard AgNO₃ solution. When all this work was completed then the 60ml solution was kept on a magnetic stirrer and a magnetic bar is used for stirring inside the solution. Then while stirring 1ml of AgNO₃ solution was added slowly with the help of a siring. This solution was kept on a magnetic stirrer for 1hr. and then gradual darkening of the solution was formed as a function of the amount of silver nitrate added to the solution. Similarly, 2ml, 3ml, 4ml, and 5ml concentration of AgNO₃ solution was added to the more four same amount of 60ml solution and this solution was also kept on a magnetic stirrer for 1hr as shown in Fig.2(a) and (b).
Fig 2. Synthesis of silver nanofluid and measurement of ultrasonic velocity

Thus the probable reaction mechanism for the formation of Ag nanoparticles by tannic acid reduction of AgNO₃ can be represented as below:

\[
\text{(Phenolic form)} \quad \text{Phenol} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \\
\text{(Quinone form)} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O}
\]

\[
\text{Ag}^+ + 2\text{e}^- \rightarrow \text{Ag}_0
\]

In this model reaction, phenol took part in redox reactions to form quinones and donate electrons. The Ag⁺ converted to be Ag atoms followed by electrons, forming Ag clusters, and producing Ag-particles by cluster growth. Ag atoms are stabilized from oxidative reactions and aggregations when capping in tannin molecules.

4. UV-Vis spectroscopy measurements

The absorption spectrum of synthesized silver nanofluid for different concentration was observed by ultraviolet-visible spectrophotometer (HITACHI). Fig.3 shows the UV-Vis absorption spectra of silver nanofluid scanned in the wavelength range of 300 - 600 nm. The strong absorption peaks of UV-visible spectrum revealed the presence of silver nano particles. The UV-visible spectrum shows strong absorption peaks at 410 nm and 416 nm due to the plasmon oscillation modes of conduction electrons in the colloidal nanoparticles-liquid suspensions. This indicates that size of Ag nanoparticles increases with increase of
concentration. The peak shifting towards the shorter wavelength region was observed indicating the
decrease in the size of nanoparticles.

![Absorbance vs. Wavelength](image)

Fig 3. Absorption spectra of silver nanofluids

4. Ultrasonic velocity measurements

Ultrasonic velocity measurements have been made at 2 MHz of frequency with help of a variable
path interferometer at temperature 30°C. The temperature stability is maintained within 0.1K by
circulating thermo stated water around the interferometer cell that contains the sample, with circulating
pump. The velocity of ultrasonic waves in the liquid is calculated as

\[ C = \frac{f \lambda}{2} \]  \hspace{1cm} (1)

where \( f \) is the frequency of the generator and \( \lambda \) is the wave length of ultrasonic wave measured from the
interferometer. The measured ultrasonic velocity data and density of nano fluid are used to compute the
acoustical parameter such as adiabatic compressibility (\( \beta \)), intermolecular free length (\( L_f \)) and acoustic
impedance (\( Z \)) using relations [9]

\[ \text{Adiabatic compressibility, } \beta = \left( \rho C^2 \right)^{-1} \]  \hspace{1cm} (2)
\[ \text{Intermolecular free length, } L_f = k\beta^{1/2} \]  \hspace{1cm} (3)
\[ \text{Acoustic impedance, } Z = \rho C \]  \hspace{1cm} (4)

The constant \( k \) is temperature dependent which is given as [93.875 + (0.375T)] ×10^8 and ‘T’ being the
absolute temperature.
5. Result and discussion

![Ultrasonic velocity vs Concentration of nanofluid](image)

Fig 4. Variation of ultrasonic velocity with concentration of silver nano fluid

From Fig.4 it is found that ultrasonic velocity increases with increase in concentrations of nanofluids. But at certain concentrations it shows variation in the values. The increase in velocity with increase in mole fraction of particles is due to structural changes occurring in the liquid system which results in weakening of intermolecular forces. The gradual increase in velocity up to 2ml Ag nanofluid concentration is due to interaction between Ag⁺ ions and water molecules. Increase in velocity in solution indicates that the interaction may be due to the surface effect because of hydrogen bonding between particles and water molecules. Hence, there might be particle fluid interaction which favors increase in the velocity values. The random movements of nanoparticles are increased with increase in concentration and when the ultrasonic vibration is propagated in nanofluid, Brownian motion stops the fluid particles in suspension, leading to decrease in velocity. Therefore, at higher concentrations it is found that there is deviation in ultrasonic velocity. Also agglomeration in particles leads to collisions between the suspended particles.

![Acoustic impedance vs Concentration of nanofluid](image)

Fig 5. Variation of acoustic impedance with concentration of silver nano fluid

It is also observed that at 2ml concentration, there is a decrease in velocity value which suggests that there may be weak interactions between particles and water molecules. The structural changes affect the
compressibility and hence there is a change in ultrasonic velocity. The decreased velocity value shows that there is decrease in nanoparticle-fluid interaction and increase of particle–particle interaction. Thus it may suggest that, the ultrasonic velocity is quite sensitive to the size, morphology and dispersion of the particles. The increase in density with concentration is due to interactions between particles and water molecules.

It is observed that acoustic impedance values increases with increase in concentration of particles and then it decreases with further increase in concentration. It implies that the Z-values show similar behavior to that of ultrasonic velocity values as shown in Fig.5. From the profile it is observed that acoustic impedance increases with increase in Ag⁺ ion concentrations in water. But there is a decrease of Z-value at 2ml concentration which shows weak interactions similar to ultrasonic velocity. The higher values of acoustic impedance indicate that there is a significant interaction between the particle and base fluid molecules which may affect the structural arrangement. The interaction between particles and base fluid molecules increases the intermolecular distance between the molecules which in turn causes impedance in the propagation of ultrasonic waves.

![Fig 6. Variation of adiabatic compressibility with concentration of silver nano fluid](image)

![Fig 7. Variation of intermolecular free length with concentration of silver nano fluid](image)

It is also found that the adiabatic compressibility and free length decreases with increasing concentration of particles. The decrease in adiabatic compressibility and free length shows (Fig.6 and Fig.7) the weaker
force of interaction between particles and base fluid molecules. Compressibility decreases due to the fact that Ag⁺ ions form a core compact structure with the solvent molecules through hydrogen bonding. Deviations in the values of adiabatic compressibility and intermolecular free length exhibit in the system may be due to weak forces operating with some specific interaction between molecules in this. Decrease in free length value causes rise in sound velocity in the system which is an indication of clustering together of the molecules into agglomerates.

6. Conclusion

In the present paper silver nanoparticles are obtained using one step chemical method. From ultraviolet-visible spectrophotometer analysis, the nano size confirmed comparing with the literature data [10-11] and particle size of silver nano particle with tannic acid at room temperature is greater than 15nm. Homogeneous suspensions of silver nanofluids are prepared in different concentrations with the aid of magnetic stirrer. Ultrasonic velocity studies were carried out for the prepared nanofluids at room temperature (303K). The acoustical parameters including adiabatic compressibility, intermolecular free length, and acoustic impedance are calculated for all the samples. Interaction between nanoparticles and water molecules was analyzed using acoustical parameters. The ultrasonic studies provide comprehensive investigations between Ag⁺ ion and water molecules. From the analysis, it is evident that the particle–fluid interaction in microfluids decreases with increasing particle loading [12]. But for the nanofluids the particle –fluid interaction increases with increase of concentration up to a critical concentration of 2ml above which the particle –fluid interaction weakens due to strong particle – particle interaction. It is observed that there is particle – fluid interaction which favors increase in velocity. Thus, particle–fluid interaction studies are helpful to understand the reasons behind anomalous enhancements in physical properties of nanofluids in nanoscale.

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