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Ultrasonic study of Au-nanoparticles-liquid suspensions

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ABSTRACT

The absorption and velocity of ultrasound were studied for colloidal solution of gold (Au)-nanoparticles in polymer molecules refreshed reactive nascent surfaces of N- polyvinyl pyrrolidone (PVP) in an aqueous solution. The average size of Au-nanoparticles could be varied in 4-10 nm range by conducting the reaction at an elevated temperature 50-60°C. The frequency used were 5-25 MHz and 2 MHz for absorption and velocity at concentration range 0.5-1.0 wt% of Au-PVP samples in between 5-70^{0}C temperature. The results demonstrate that the primary reaction during the Au-nanoparticles-PVP colloidal formation occurs in divided groups in small micelles for the two lower concentrations 0.05 & 0.1 wt%. The results are analyzed for predicting the enhanced thermal conductivity of the samples and discussed in correlation with optical and electrical properties.

KEYWORDS

Nanofluid;
Ultrasonic velocity;
Ultrasonic attenuation;
Thermal conductivity;
Pulse-echo-technique.

INTRODUCTION

Recently, there have been a limited number of studies on ultrasonic properties of nanofluids[1,2]. Since nanofluids are expected to use under flow conditions, the ultrasonic NDT studies of the nanofluid is an emergent field. When crystalline solids with nanometer dimensions are suspended in a suitable base fluid to form stable homogeneous suspensions, and there is an increase in the thermal conductivity relative to the base fluid, the resulting suspensions are called nanofluids[3,4]. Nanofluids derived by dispersing nanoparticles of gold metal in organic compound in a polymer composite structure have attracted a great deal of interest in scientific research and industrial applications owing to their unique fugacity, activity, reactivity and other useful optical or electrical properties for biosensor, catalysts or other applications. In particular, gold metal of such small particles mixes up in selected organic compounds such as polyvinyl alcohol (PVA), PVP in a simple dispersion reaction in a common solvent such as water, resulting in useful nanofluids of present interest.

The acoustic properties of heterogeneous media with a continuous fluid phase have been of interest in numerous applications, such as predicting the effectiveness of foghorns and describing the acoustics of bubbly and two-phase flows that are encountered in the process and the nuclear power generation industries. More recently there has been an increasing interest in the acoustic properties of suspensions for acoustic telemetry through

drilling fluids, as well as a rising demand for ultrasonic particle size and concentration instrumentation. Commercial instruments have been developed to characterize the properties of suspensions using ultrasound[5]. Non-linear optical properties of colloidal Au and PVP composite were investigated using Z-scan technique 25 ps pulses at 532 nm near the surface plasmon resonance frequency of Au nanoparticles by Hong Shen et al.[6]. Several workers have made the studies on the suspension of solids in a liquid aiming to identify the mechanism that enable useful information to be extracted from the ultrasonic velocity and attenuation information such as particle size, concentration and thermophysical properties of the constituents[7-10]. Recently, there has been significant interest in the preparation of metallic nanoparticles with various compositions, structures, shapes and sizes[11-14]. Due to their unusual chemical and physical properties, they are expected to have potential applications in many technologies, such as optoelectronic nanodevices, catalysts and chemical sensors[15]. Polymers have been found to effective stabilizers of colloidal metal nanoparticles. In the present investigation, PVP is used as the matrix substance for the suspension of various gold nanoparticles.

In the present work we report our novel results of the studies of the ultrasonic attenuation and velocity in a polymer colloidal solution with dispersed Au-metal nanoparticles. The colloid solutions used here have been developed by in-situ dispersion and reduction of Au^{3+} cations to Au-metal of divided nanoparticles in polymer molecules of refreshed reactive nascent surfaces of PVP in an aqueous solution at an elevated temperature. The result are analyzed and discussed in correlation with the microstructure and thermal properties.

EXPERIMENTAL

A freshly prepared homogeneous colourless transparent PVP solution in water has been used. It was obtained by dissolving 3.0 g PVP in 100 ml of double distilled water. A continuous stirring over a magnetic stirrer at a constant temperature of 50-60^{0}C promotes the PVP dissolution in water in a clear solution. An aqueous $AuHCl_4.3H_2O$ solution of 1.0 M concentration has been selected to derive an Au-PVP colloidal solution. Adding $AuHCl_4.3H_2O$ solution to the PVP solution while stirring the total solution carries the proposed reaction. In this way, Au-PVP solutions of selected Au contents of 0.05, 0.1, 0.2, 0.5, and 1.0 g in 100ml total solutions were prepared. Here, a simple reaction of Au^{3+} cations, from a gold metal salt such as $AuHCl_4.3H_2O$ with PVP (average molecular weight 40,000 and polymerisation number n = 360 according to PVPk30) in ionised water is developed to derive the Au-PVP nanofluids. They were used as stock solutions to perform the proposed ultrasonic velocity and ultrasonic attenuation studies.

The velocity measurements have been made by a standard variable path interferometer technique at 2 MHz. The temperature variation was accurate to ±0.5^{0}C and velocity to ±0.1%.

Standard pulse-echo technique (PET) has been used for ultrasonic absorption measurements at different frequencies. Pulses are sent by a 5-25 MHz quartz crystal and decay is observed on the cathode ray oscillograph. The decay is made exponential by adjusting the levelling screws and adjusting the crystal and the reflector parallel to each other. The ultrasonic intensity decreases exponentially with the path length. Thus the intensity at particular distance between the quartz crystal and the reflector in the experimental arrangement can be written as:

$$I_x = I_0 e^{-2\alpha X} \quad (1)$$

where x is twice the distance between quartz crystal and the reflector. I_0 is the maximum intensity and 'α' is the absorption coefficient. If I_{X1} and I_{X2} are the intensities of ultrasonic waves at x_1 and x_2 distances from quartz crystal then from Equation (1) one can write the following expressions.

$$I_{X1} = I_0 e^{-2\alpha X_1} \quad (2)$$

$$I_{X2} = I_0 e^{-2\alpha X_2} \quad (3)$$

On solving the eq. (2) and (3) one can easily obtain the following expression for the ultrasonic attenuation.

$$\alpha = \frac{1}{2(X_2 - X_1)} \log \frac{I_{X_2}}{I_{X_1}} \quad (4)$$

The absorption coefficient is calculated using the eq. (4). Finally we obtain the values of ultrasonic absorption coefficient over frequency square (α/f^2). Accuracy in the absorption measurement is ± 5%. Several known values of 'α' and velocity for standard liquids were justified so as to have satisfaction in absorption

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and velocity measurements. The observations were repeated several times.

RESULTS AND DISCUSSION

Physical properties of polymeric colloids

When adding an $AuHCl_4.3H_2O$ solution (0.05 to 1.0 M concentration) to a PVP solution (3.0g/100ml) in water, a polymer complex form by a redox reaction of $AuHCl_4$ with the PVP polymer molecules of refreshed reactive nascent surfaces caused during the processing using the mechanochemical attritions under heating conditions of the solution. The reaction occurs in steps, depending on the initial concentrations in the two solutions and other experimental conditions. Ultimately, a colloidal solution consisting of gold metal nanoparticles embedded in a moiety of modified PVP polymer molecules appears in a colloid complex in a characteristic equilibrium colour. The occurrence of a stable coloured polymer complex in this reaction is indicative of formation of an inorganic-organic colloid of a stable microstructure. The photograph of the color of the samples is shown in figure 1.

Following our experimental observation, it is proposed that the reaction process involves a cross-linking of PVP in a specific polymer structure of an enhanced viscosity of the average value in the two reaction components of (i) $AuHCl_4$ solution and (ii) the PVP polymer solution.

The crystal structure of the Au- nanoparticles dispersed in this polymer complex is examined with X-ray diffraction. The colloid sample dispersed over a glass plate has been used to measure the X-ray diffraction. According to it, the Au-nanoparticles occur in the usual fcc crystal structure (F_{m3m} space group) of lattice constant a = 0.414nm, which compares the bulk value of a = 0.408nm[16]. Most of the Au-particles represent single crystallites of a triangular, rectangular or a hexagonal shape as studied with the microstructure using a transmission electron microscope. The Au crystallites are found to be as small as 4 to 10 nm of average diameter. A similar dimension of Au–crystallites has been reported earlier, for example see Gupta et al.[17], in other Au colloids or composites.

Figure 1 : Photograph of the color of the samples, (1) 3.0 wt% PVP, (2) 0.05wt% Au-PVP, (3) 0.1 wt% Au-PVP, (4) 0.2 wt% Au-PVP, (5) 0.5 wt% Au-PVP, (6) 1.0 wt% Au-PVP

Ultrasonic velocity and ultrasonic attenuation

As the ultrasonic velocity is highly sensitive to the local structure, we applied it here to examine its value in our Au-PVP polymer colloids at selected temperatures in the 5-70C range. The results are shown in figure 2. The plot of the ultrasonic velocity as a function of the temperature passes through a minimum and maximum at 48°C and 54°C for 0.05 and 0.1 wt% Au-PVP samples. For other samples the velocity increases up to 48°C and then remains constant.

Figure 3-5 show a typical plot of ultrasonic absorption in the samples with 5-25 MHz frequencies and at different temperatures from 5-70°C. As expected the temperature dependency of the ultrasonic absorption in the samples is found to the reversal of the behaviour of the temperature dependency of the ultrasonic velocity in the samples.

In the present work, the temperature dependence of the ultrasonic velocity as well as the ultrasonic attenuation does not follow a linear curve through the temperature range. This seems to be in a contrary to the results in a sample of pure gold metal. In general, as in other materials[18], both the ultrasonic velocity and the ultrasonic attenuation are quite sensitive to the particles size, morphology and dispersion of the particles. A macroscopic interaction of Au particles with the PVP polymer molecules appears to be a critical parameter to control their final values in this specific example of an inorganic-organic polymer nanocolloidal solution.

The effective attenuation in this example can be expressed as:

$$\alpha = \alpha_p + \alpha_m + \alpha_{pm}$$

where α_p is the contribution from the Au-nanoparticle, α_m is the counterpart contribution from the polymer matrix, α_{pm} describes the change in the final α-value owing to a macroscopic interaction between the two components in an Au-PVP nanocolloid structure and

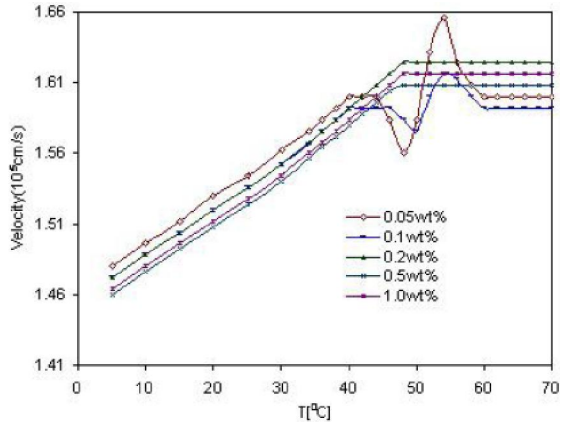

Figure 2 : A plot of ultrasonic velocity in different concentration Au-PVP polymer samples as a function of temperature

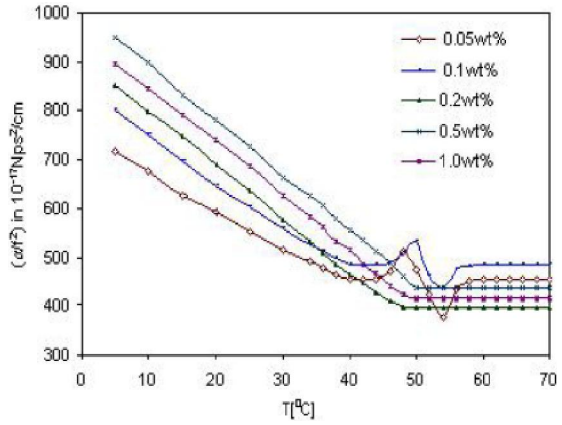

Figure 3 : A plot of ultrasonic absorption at 5MHz in different concentration Au-PVP polymer samples as a function of temperature

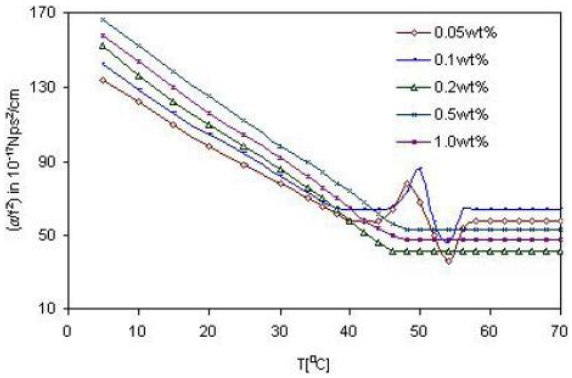

Figure 4 : A plot of ultrasonic absorption at 15MHz in different concentration Au-PVP polymer samples as a function of temperature

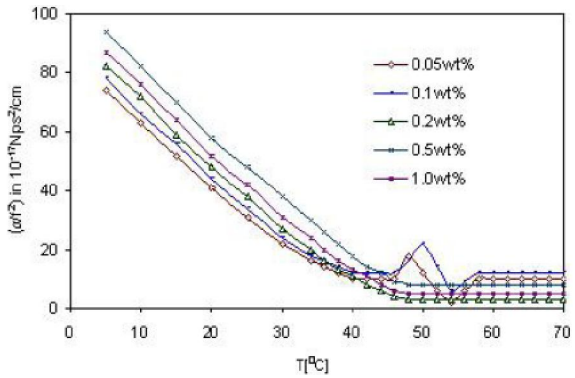

Figure 5 : A plot of ultrasonic absorption at 25MHz in different concentration Au-PVP polymer samples as a function of temperature

associated modified thermophysical properties of the nanofluid.

The parameter α_{pm} includes the effects of the modified electronic structure of the specimen. The Au-PVP polymer composite electronic structure is a complex function of size, morphology and topology in Au-metal nanoparticles and those in the surrounding PVP polymer molecules. Occurrence of a stable Au-PVP surface interface is another crucial physical parameter to determine the final α_{pm} value.

Biwa et al.[7] analysed the ultrasonic attenuation in mm sized particles-reinforced polymers by a differential scheme and found good agreement between the theory and experiments. The significant attenuation due to scattering by the particles-reinforced was incorporated in the total attenuation in their theoretical model. The observed attenuation in our case could not be explained by the exact theoretical model following the differential scheme. We found that the attenuation due to scattering from the Au-nanoparticles in the nanofluid (Au + PVP) is not significant. It is also important to note that the characteristic behaviour of the ultrasonic attenuation in the Au+PVP nano-colloids is not found in any of the individual components of the composite[19,2]. Calculated value of the ultrasonic attenuation in the sample (0.05wt% Au-nano particles suspended in PVP) for 5 MHz at 48°C following the differential scheme including the ultrasonic absorption due to nanoparticles and thermo-elastic loss becomes 92.44×10^{-3}Np/cm. Here the thermal conductivity 'K' of the nanoparticles for the calculation of thermo-elastic loss $[3K/C_V(\overline{v})^2]$ has been taken following the molecular dynamics method. $\overline{v}$ denotes the Debye average velocity of the wave and C_V denotes the specific heat per unit volume. The total observed attenuation in our experiment for

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the sample is 128×10^{-3} Np/cm. Also it is clear that the attenuation is directly proportional to the thermal conductivity[20].

Thus, it is very interesting to predict the cause behind the excess attenuation in the present experimental value.

Most importantly scientists have been perplexed by the thermal phenomena behind the recently discovered nanofluids like the present studied material. One fascinating feature of nanofluids is that they have anomalously high thermal conductivities at very low nanoparticles concentrations[21-23]. They have found that the Brownian motion of nanoparticles at the molecular and nanoscale level is a key mechanism governing the thermal behaviour of nanoparticles-fluid suspensions (nanofluids). Choi et al.[22] proposed the theoretical model that accounts for the fundamental role of dynamic nanoparticles in the nanofluids. They have derived a general expression for the thermal conductivity of nanofluids involving different modes of energy transport in the nanofluids. The important mode is thermal interaction of dynamic or dancing nanoparticles with base fluid molecules. Even though the random motion of nanoparticles is zero when time averaged the vigorous and relentless interactions between liquid molecules and nanoparticles at the molecular and nanoscale level translate into conductions at the macroscopic level, because there is no bulk flow.

Although the fourier transform infrared (FTIR) spectroscopy results of Au+PVP are not available to compare but the FTIR results for some like materials-Ag-nano+PVA are available in the literature[24-26]. In FTIR results of Ag-nano+PVA, disappearance of several bands (837, 711, 650 and 570 cm^{-1}) on increase in the Ag-nano filler content in PVA+Ag suggests that the interaction between Ag-nano particles and the matrix PVA takes place.

Thus we may postulate that the Brownian motion of nanoparticles in nanofluids produces convection like effects at the nanoscale. Moreover, the thermal conductivity model not only captures the concentration and temperature dependent conductivity, but also predicts strongly size-dependent conductivity. The concentration and temperature dependent conductivity data for the present nanofluid are not available in the literature. We can predict the anomalously increased concentration / temperature dependent thermal conductivity of Au-nano+PVP nanofluid on the basis of observations on FTIR in other like materials[24-26]. As we know, thermo-elastic ultrasonic attenuation is directly proportional to the thermal conductivity of the composite.

CONCLUSIONS

Following conclusions have been made as:

- A chemical dispersion of Au-metal nanoparticles in an aqueous solution of PVP polymer molecules forms a stable colloidal solution with stable optical and ultrasonic properties.
- The concentration and microstructure of Au-metal additives determine the chemical stability and in turn stable and reproducible chemical and physical properties in the resultant composite structure.
- The Au-PVP polymer colloids, developed through a novel chemical method involving a reaction of dispersed Au^{3+} cations with PVP polymer molecules of refreshed reactive nascent surfaces, offer specific applications as optical materials, biomaterials and sensors.
- The effective increased thermal conductivity of the present nanofluid due to Brownian motion of the nanoparticles appears as the cause behind the excess attenuation in the present observed experimental value.
- The achieved results in the present investigation can be used for further study using other methods such as electron microscope (SEM, TEM), optical devices, X-ray scattering, surface tension, viscosity, FTIR spectroscopy and various transform phenomenon. These results expend future prospects for the application of Au-PVP nanofluids.

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