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Synthesis of Calcium Fluoride Nanoparticles by Chemical Route for Ultrasonic Investigations

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ABSTRACT

The main objective of this research work is to synthesize calcium fluoride nanoparticles by the chemical route and to measure the ultrasonic velocity, density, and viscosity of methanol-based calcium fluoride nanosuspension. The prepared Calcium Fluoride (CaF_2) was characterized by X-ray Diffractometer (XRD) analysis, Scanning Electron Microsopy (SEM) and it is found that the average particle size is of the order of 48nm. Ultrasonic velocity measurements were carried out by the Interferometer technique operated at 1 MHz frequency at a low concentrations varied from 0.002 to 0.1 wt/vol% of calcium fluoride nanoparticles in methanol at a temperature 25°C to 40°C. It helps in finding out many other acoustical parameters such as adiabatic compressibility, acoustic impedance, free volume, free length, and relaxation time. All these acoustical parameters are highly reflect the information of interaction that occured between Ca^{2+} ions and dispersion medium(methanol). It is observed that ultrasonic velocity increases with an increase of nanoparticles weight fraction in methanol, and shows a peak at a concentration of 0.002 wt/vol% and deep at a concentration of 0.006 wt/vol%. It may be due to the ion-dipole interaction between Ca^{2+} ions and methanol molecule, which is strong.

Keywords: Calcium Fluoride Nanoparticles; X-ray Diffractometry; Scanning Electron Microscopy; Ultrasonic Velocity; Ion-Dipole Interactions

INTRODUCTION

Nanoparticles are routinely defined as anything with a particle size of the order of 100nm that shows properties that are not found in bulk samples of the same material. The synthesis of nanoparticles and the study of their properties are of fundamental importance in the advancement of recent research. It is found that the optical, electronic, magnetic, and catalytic properties of metal nanoparticles depend on their size, shape, and chemical surroundings [1, 2]. In nanoparticles synthesis, it is very important to control not only the particle size but also the particle shape and morphology as well. In the present investigation, the synthesis of Calcium fluoride by chemical route is discussed, which is an easy, simple, cost-effective, and convenient route for preparing nanoparticles [3, 4]. It is easy to control synthesis parameters and yield a large number of samples.

Low solubility and wide transmission make calcium fluoride extremely useful for a variety of different applications including microlithography, mirror substrates for UV laser systems, windows, lenses, and prisms for UV and IR applications. A polished calcium fluoride surface can be expected to withstand several years of exposure to normal atmospheric conditions [5]. Due to its high transmission, it is also used in spectroscopic windows, lenses, and for the design of vacuum furnaces.

The acoustic properties of particle-fluids interaction are investigated by ultrasonic interferometer techniques. The method is also used for the investigation of structure changes under the influence of different temperatures and concentrations. Only by ultrasonic technique, weak interaction between nanoparticles suspension can be determined. The possible aggregation of nanoparticles in nano colloids plays a key role in the drug delivery system because colloidal forms of the drug are easily absorbed by the body

tissues and hence are more effective. The investigations of Ultrasonic velocity and measurement of density are the basic parameters to derive many acoustical relation such as adiabatic compressibility, isothermal compressibility, free volume, free length, acoustic impedance, and relaxation time etc. All these acoustical parameters are related to the surface of nanoparticles and nanoparticle's interaction. The ions-dipole interaction of nanoparticles causes to increase or decrease in acoustic parameters, making us to detect possible particle-base fluids interaction with the ultrasonic technique.

Ultrasound spectroscopy is very useful in the investigation of acoustic properties of nanosuspensions and has some advantages over many existing technologies because it is non-destructive and non-invasive [6]. Only by ultrasound technique, weak interaction between nanoparticles can be determined. It can provide useful information to a higher concentration than optical methods.

EXPERIMENTAL TECHNIQUE

Sample Preparation

All chemicals used were of analytical grade. Aniline, ammonium persulphate, and ammonium hydroxide from SD Fine Chemical, India. Stannic chloride and hydrochloric acid from Merk were used as received without further purification. Double distilled water was used throughout this work.

In the preparation of CaF_2, we used Calcium Chloride Dehydrate ($CaCl_2{\cdot}2H_2O$, Merk-99.9%), Nitric Acid (conc. HNO_3, Merk-99.99%), Ammonium Fluoride (NH_4F, Merk-99.50%), Bismuth Nitrate ($Bi(NO_3)_3{\cdot}5H_2O$, Merk-99.50%), and Ethanol as raw materials. The CaF_2 was prepared in the following method. Dehydrated calcium chloride was mixed into alcohol to form a transparent solution and then ammonium fluoride was added in excess to the calcium chloride solution. A whitish solution was obtained, which was then stirred for 10–12 h, after that calcium chloride was mixed completely with ammonium fluoride solution. Then ethanol was added to the solution and kept on a high-speed centrifuge at 3000 rpm for 3 h at 22-25°C, finally paste was formed in white color. This paste was dried at 60°C for 12 h to get white powder. The mean crystallite size of the sample is calculated using Scherer's formula [7],

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

Where 'λ' is the wavelength of X-ray (0.1541nm), 'W' is FWHM (full width at half maximum), 'θ' is the diffraction angle and 'D' is particle diameter (size). The average particle size of CaF_2 is found to be around 48 nm (Figure 1).

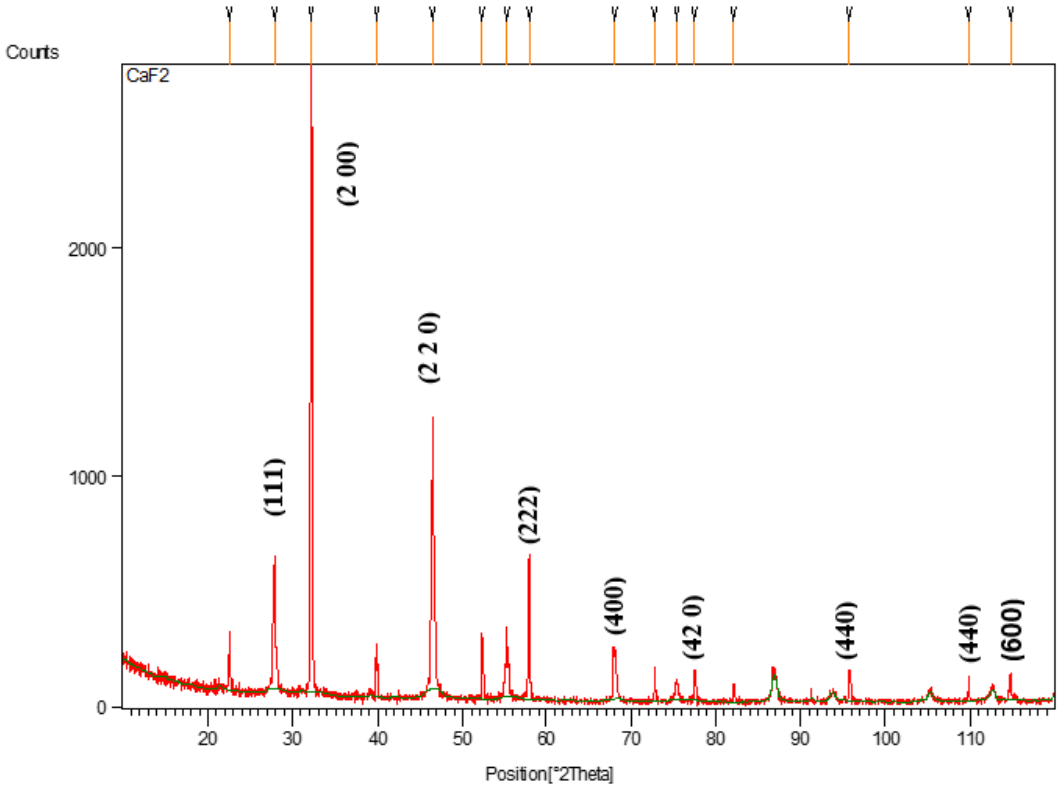

Figure 1. X-ray Diffraction pattern of CaF_2

Measurement

The X-ray diffraction of the nano-sized calcium fluoride is obtained by using a Philips Holland, PW-1710 x-ray diffractometer

having Cu kα x-ray radiation of wavelength λ=1.5405 A0 and a continuous scan of 20/ min at 35 kV and at 20mA as shown in figure 1. Ultrasonic velocity measurements were carried out using multifrequency interferometer (Mittle F-83 model) techniques at the frequency of piezoelectric transducers 1MHz. A Thermostat (Lab Slab) controls the temperature of the liquid to an accuracy of ± 0.1°C. Density measurement was carried out using specific gravity bottles and digital mono pan-balance with an accuracy of 0.001mg. The SEM photographs of prepared CaF_2 powders as shown in Figure 2.

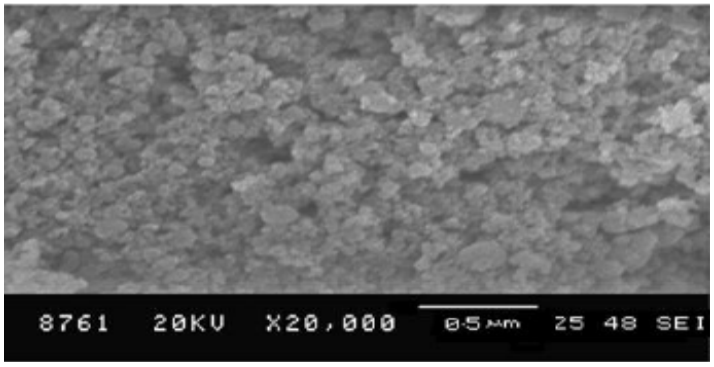

Figure 2. SEM images of synthesized CaF_2

The SEM results reveal that the powder was porous and agglomerated with polycrystalline nanoparticles. The larger particles exhibited numerous spherical perturbances on the surface, suggesting that they were formed during the precipitation process through fusion of the much smaller particles. The synthesized CaF_2 nanoparticles nanoparticles are spherical in shape while were smaller size of around 48 nm and less agglomerated (Table 1-8) [8].

Observation Table

Table 1. Measured Value of Ultrasonic Velocity, Density, Adiabatic compressibility, and Isothermal compressibility at 25°C

Concentration wt% X	Ultrasonic Velocity [m/sec]	Density [Kg/m^3]	Adiabatic compressibility [Kg^{-1}ms^2]	Isothermal compressibility [Kg^{-1}ms^2]
0	1101.5	780	1.05666 X 10^{-9}	1.58499 X 10^{-9}
0.002	1141.654	759.576	1.01009 X 10^{-9}	1.48 X 10^{-9}
0.004	1119.679	763.3415	1.04495 X 10^{-9}	1.55 X 10^{-9}
0.006	1100	765.412	1.12336 X 10^{-9}	1.65 X 10^{-9}
0.008	1120.556	766.0151	1.0268 X 10^{-9}	1.5402 X 10^{-9}
0.01	1093.111	767.9913	1.08972 X 10^{-9}	1.63458 X 10^{-9}

Table 2. Measured Value of Free volume, Free length, Acoustic Impedance and Relaxation time at 25°C

Concentration wt% X	Free volume [cm^3/mol]	Free length [A°]	Acoustic Impedance [Kg·m^{-2}s^{-1}]	Relaxation Time [sec]
0	5.85127 X 10^{-8}	6.48502 X 10^{-11}	859170	7.71 X 10^{-12}
0.002	3.91897 X 10^{-5}	6.34049 X 10^{-11}	867172.9787	1.00049 X 10^{-11}
0.004	3.73774 X 10^{-5}	6.44896 X 10^{-11}	854697.4436	1.05065 X 10^{-11}
0.006	3.64053 X 10^{-5}	6.68655 X 10^{-11}	809261.9348	1.13253 X 10^{-11}
0.008	4.14689 X 10^{-5}	6.39273 X 10^{-11}	863724.9551	1.03401 X 10^{-11}
0.01	4.27783 X 10^{-5}	6.58568 X 10^{-11}	839499.7298	9.86002 X 10^{-11}

Table 3. Measured Value of Ultrasonic Velocity, Density, Adiabatic compressibility, and Isothermal compressibility at 30°C

Concentration wt% X	Ultrasonic Velocity [m/sec]	Density [Kg/m^3]	Adiabatic compressibility [Kg^{-1}ms^2]	Isothermal compressibility [Kg^{-1}ms^2]
0	1085.8	774	1.09587 X 10^{-9}	1.64381 X 10^{-9}
0.002	1137.667	754	1.0247 X 10^{-9}	1.53706 X 10^{-9}
0.004	1113.111	760.3369	1.06149 X 10^{-9}	1.59224 X 10^{-9}
0.006	1090.693	761	1.14438 X 10^{-9}	1.71657 X 10^{-9}
0.008	1114	762.892	1.05625 X 10^{-9}	1.58437 X 10^{-9}
0.01	1080.556	763.5114	1.12173 X 10^{-9}	1.6826 X 10^{-9}

Table 4. Measured Value of Free volume, Free length, Acoustic Impedance and Relaxation time at 30°C

Concentration wt% X	Free volume [cm^3/mol]	Free length [A°]	Acoustic Impedance [Kg·m^{-2}s^{-1}]	Relaxation Time [sec]
0	6.18185 X 10^{-8}	6.60424 X 10^{-11}	840409.2	7.60 X 10^{-12}
0.002	5.00972 X 10^{-5}	6.38619 X 10^{-11}	857800.918	8.95521 X 10^{-12}
0.004	4.30002 X 10^{-5}	6.49982 X 10^{-11}	846339.3646	9.66386 X 10^{-12}

0.006	4.06899 X 10^{-5}	6.74882 X 10^{-11}	801175.7105	1.06217 X 10^{-11}
0.008	4.51594 X 10^{-5}	6.48375 X 10^{-11}	849861.6896	9.36776 X 10^{-12}
0.01	5.08142 X 10^{-5}	6.68171 X 10^{-11}	825016.8464	8.9453 X 10^{-12}

Table 5. Measured Value of Ultrasonic Velocity, Density, Adiabatic compressibility and Isothermal compressibility at 35°C

Concentration wt% X	Ultrasonic Velocity [m/sec]	Density [Kg/m^3]	Adiabatic compressibility [Kg^{-1}ms^2]	Isothermal compressibility [Kg^{-1}ms^2]
0	1070.1	770	1.13412 X 10^{-9}	1.70119 X 10^{-9}
0.002	1122.333	750	1.05851 X 10^{-9}	1.58777 X 10^{-9}
0.004	1102.632	755.6488	1.08848 X 10^{-9}	1.63271 X 10^{-9}
0.006	1074.444	756	1.18091 X 10^{-9}	1.77137 X 10^{-9}
0.008	1105	757.6592	1.08094 X 10^{-9}	1.62141 X 10^{-9}
0.01	1071.778	758.3551	1.14794 X 10^{-9}	1.7219 X 10^{-9}

Table 6. Measured Value of Free volume, Free length, Acoustic Impedance and Relaxation time at 35°C

Concentration wt% X	Free volume [cm^3/mol]	Free length [A°]	Acoustic Impedance [Kg·m^{-2}s^{-1}]	Relaxation Time [sec]
0	6.71477 X 10^{-8}	6.71851 X 10^{-11}	823977	7.33 X 10^{-12}
0.002	5.37138 X 10^{-5}	6.49069 X 10^{-11}	841749.75	8.3911 X 10^{-12}
0.004	4.98967 X 10^{-5}	6.58192 X 10^{-11}	833202.5199	8.88949 X 10^{-12}
0.006	4.75045 X 10^{-5}	6.8557 X 10^{-11}	788130.1247	9.73852 X 10^{-12}
0.008	5.19951 X 10^{-5}	6.55909 X 10^{-11}	837213.4146	8.65641 X 10^{-12}
0.01	5.89141 X 10^{-5}	6.7593 X 10^{-11}	812788.3282	8.2273 X 10^{-12}

Table 7. Measured Value of Ultrasonic Velocity, Density, Adiabatic compressibility and Isothermal compressibility at 40°C

Concentration wt% X	Ultrasonic Velocity [m/sec]	Density [Kg/m^3]	Adiabatic compressibility [Kg^{-1}ms^2]	Isothermal compressibility [Kg^{-1}ms^2]
0	1054.4	764	1.17732 X 10^{-9}	1.76599 X 10^{-9}
0.002	1080.667	747.6	1.14537 X 10^{-9}	1.71806 X 10^{-9}
0.004	1060.276	752	1.18289 X 10^{-9}	1.77433 X 10^{-9}
0.006	1058.22	753.5506	1.21872 X 10^{-9}	1.82809 X 10^{-9}
0.008	1076	752.9708	1.14709 X 10^{-9}	1.72063 X 10^{-9}
0.01	1067.719	753.8598	1.16358 X 10^{-9}	1.74537 X 10^{-9}

Table 8. Measured Value of Free volume, Free length, Acoustic Impedance and Relaxation time at 40^{0}C

Concentration wt% X	Free volume [cm^3/mol]	Free length [A°]	Acoustic Impedance [Kg·m^{-2}s^{-1}]	Relaxation Time [sec]
0	7.19695 X 10^{-8}	6.84527 X 10^{-11}	805561.6	7.16 X 10^{-12}
0.002	5.90989 X 10^{-5}	6.75175 X 10^{-11}	807906.6494	8.1911 X 10^{-12}
0.004	5.17611 X 10^{-5}	6.86144 X 10^{-11}	797327.5521	8.65036 X 10^{-12}
0.006	5.34596 X 10^{-5}	6.96459 X 10^{-11}	775386.8738	9.1491 X 10^{-12}
0.008	5.53573 X 10^{-5}	6.75681 X 10^{-11}	810196.5772	8.48401 X 10^{-12}
0.01	6.47293 X 10^{-5}	6.8052 X 10^{-11}	804910.4616	7.80248 X 10^{-12}

RESULTS AND DISCUSSION

The ultrasound wave velocity is a significant source of information on the physical and chemical properties of fluids and suspensions. The results of temperature/concentration dependence of the ultrasonic velocity in the nano CaF_2 suspension are presented in figure 3. It shows the variations of ultrasonic velocity with an increase in the concentration of calcium fluoride nanoparticles in methanol at a temperature varied from 25°C to 40°C.

The variation in ultrasonic propagation shows analogous behavior with an increase in the concentration of calcium fluoride nanoparticles in methanol. The variation in ultrasonic velocity initially increases, exhibiting a pick at a molar concentration of 0.002 and 0.008 indicates a strong interaction between the constituents, and a dip at 0.006 molar concentrations shows the weak interactions between the constituents in methanol-based CaF_2 nanosuspension. Also with an increase in temperature, ultrasonic velocity decreases, this ultrasonic absorption is due to nanoparticles and thermo-elastic loss arises due to the Brownian motion of nanoparticles at the nanoscale level is a key mechanism governing the thermal behavior of nanoparticles colloidal-fluid suspension (nanofluids) [9]. As CaF_2 is ionic bonded compound, when ionic bonded calcium fluoride nanoparticles is dispersed in methanol, Ca^{++} ions interact with the

polar methanol through ion-dipole interaction and the strength of ion-dipole interaction is more as compared to dipole-induced dipole interaction. Also with increase in temperature, thermo-elastic loss arises due thermal agitation and hence ultrasonic velocity decreases

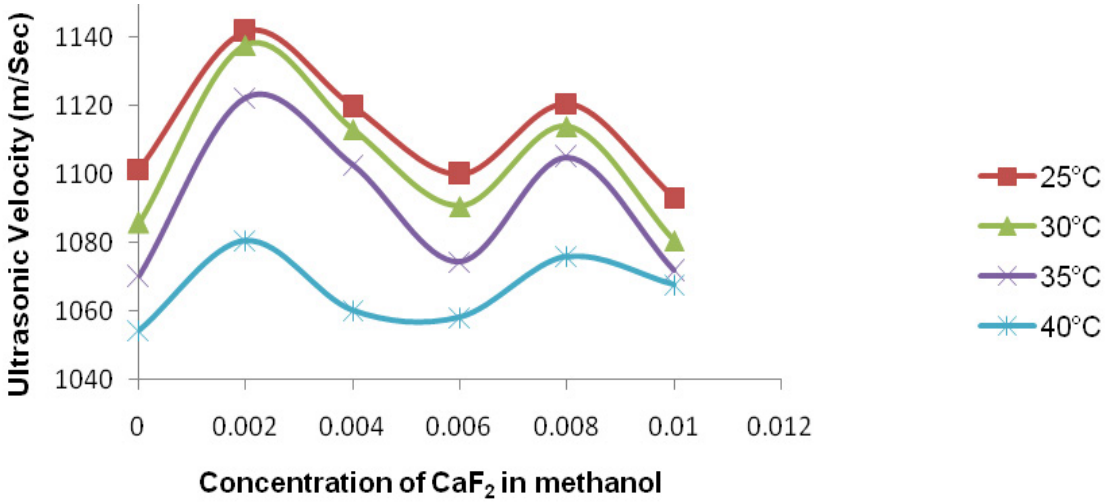

Figure 3. Variation of ultrasonic velocity with a concentration of CaF_2 in methanol

Figure 4 shows the variation of density with a molar concentration of CaF2 nanoparticles in methanol. The density of nano CaF2 suspension increases with an increase in molar concentration of CaF2 nanoparticles in methanol. This indicates the close packing between the constituents in the nanomaterial suspension.

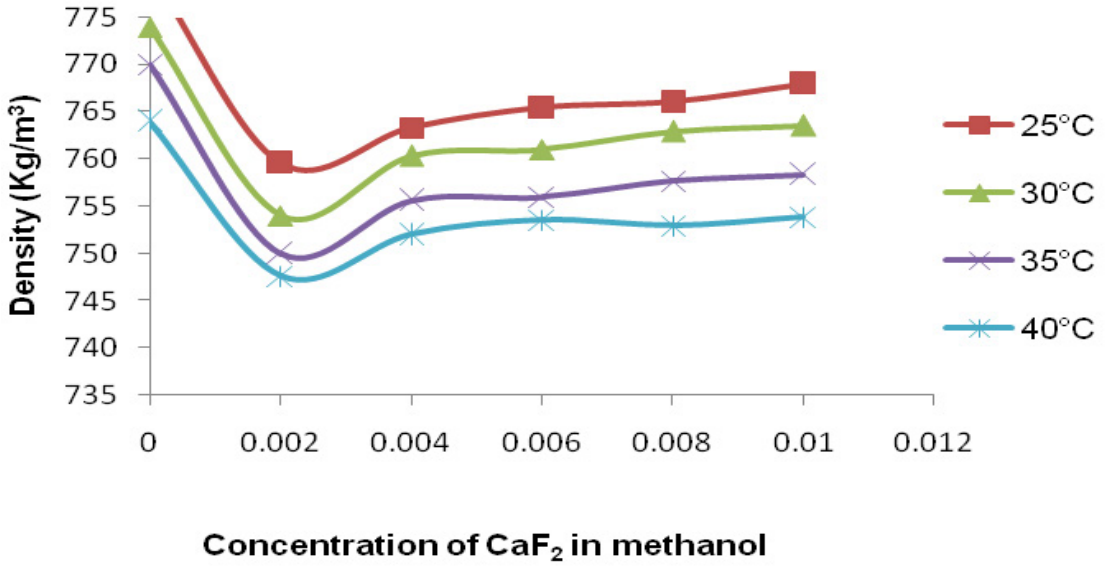

Figure 4. Variation of density with a concentration of CaF_2 in methanol

The adiabatic compressibility of a liquid is a thermodynamic parameter of fundamental significance. It enables direct access to the liquid structure in terms of the particle packing density and the inter-particle forces. According to the well-known Newton–Laplace equation β=(1/〖ρv〗^2). The adiabatic compressibility of a fluid is related to its density ρ and sound velocity v. Hence, ultrasound velocity measurements offer a favorable method to determine the compressibility.

The adiabatic compressibility shows the reverse trends as that of ultrasonic velocity which is theoretically accepted as shown in figure 5. It is observed that as the molar concentration of calcium fluoride nanopowder in methanol increases, adiabatic compressibility decreases initially and it shows a dip at molar concentrations 0.002 and 0.008. This indicates the strong particle-fluids interaction between the constituents of nanosuspension. It is termed as association in the constituents of nanosuspension. There is a peak at a molar concentration of 0.006; this indicates the weak partile-fluids interaction. It is termed as dissociation in the constituents of nanosuspension as shown in Figure 6.

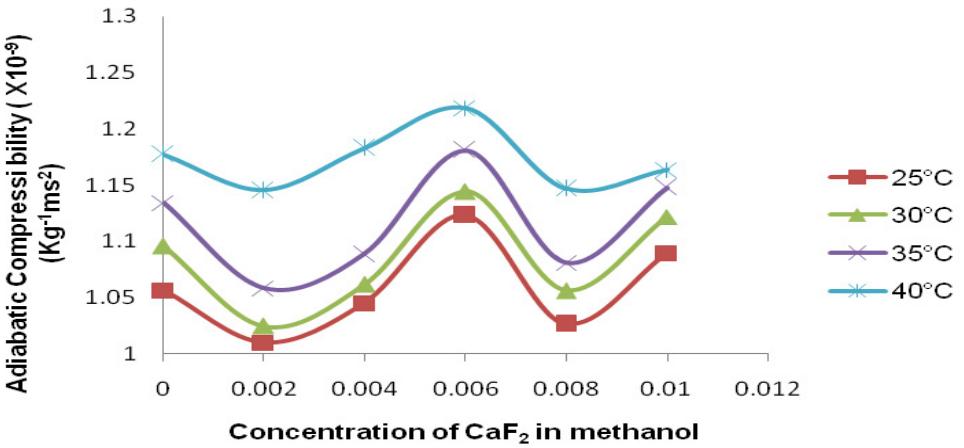

Figure 5. Variation of adiabatic compressibility with a concentration of CaF_2 in methanol

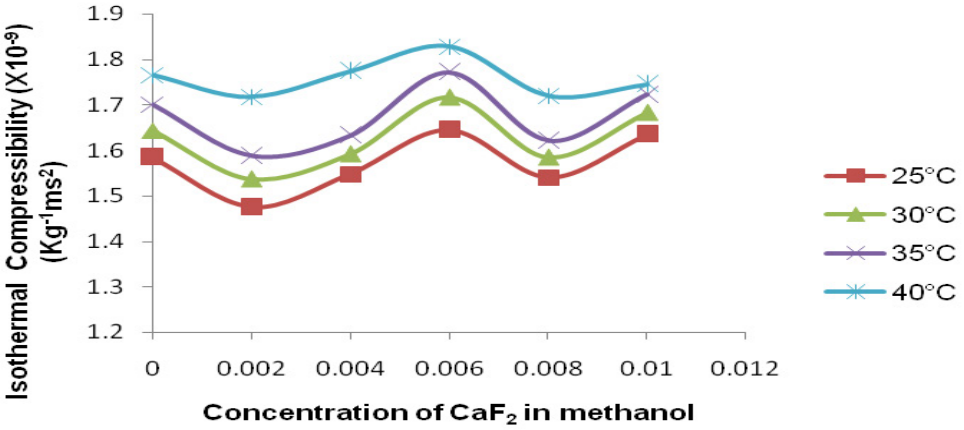

Figure 6. Variation of isothermal compressibility with concentration of CaF_2 in methanol

Figure 7 shows the variation of free volume with a molar concentration of CaF_2 nanoparticles in methanol. It indicates the closed packing of constituents of the CaF_2 nanoparticle suspension. An increase in free volume shows the increase in the magnitude of interaction. Figure 8 shows the variation of free length with a molar concentration of CaF_2 nanoparticles in methanol. As the molar concentration of CaF_2 in methanol increases, free length decreases and it shows deep at a molar concentration of 0.002 and 0.008. This indicates association and strong interaction between solute and solvent. At a molar concentration of 0.006, it shows the peak. This indicates molecular dissociation and weak interaction between solute and solvent.

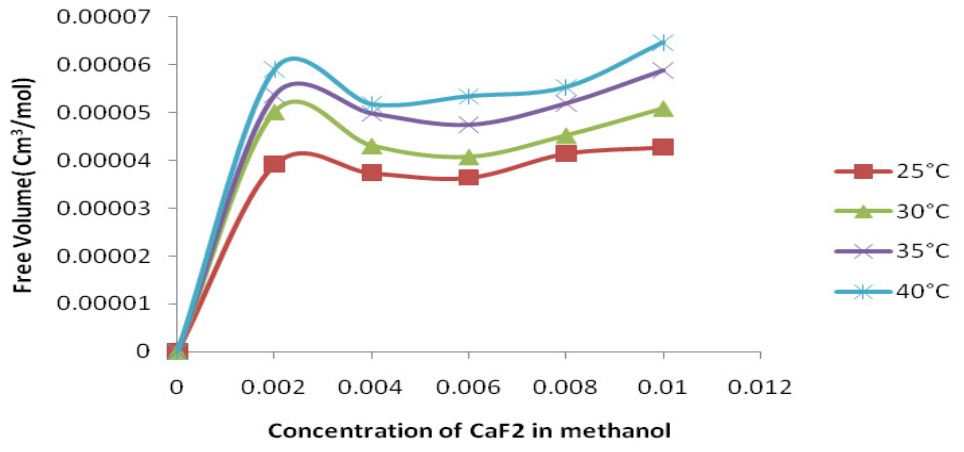

Figure 7. Variation of free volume with concentration of CaF_2 in methanol

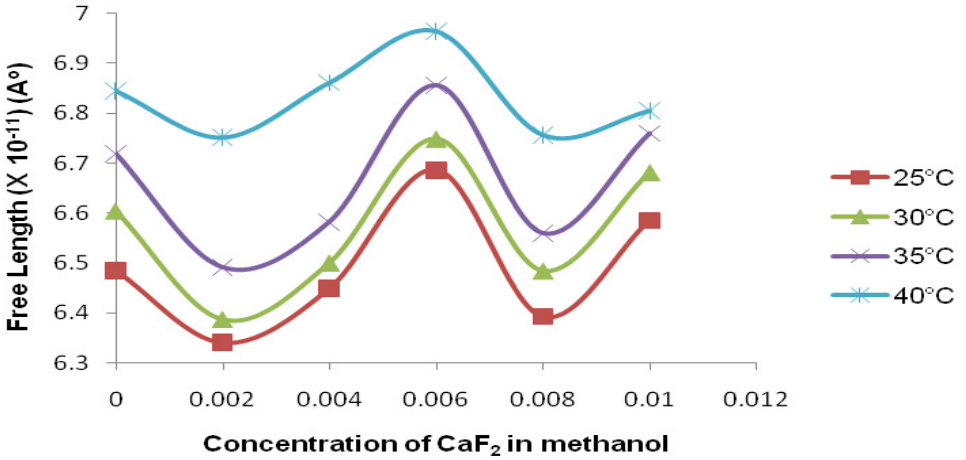

Figure 8. Variation of free length with concentration of CaF_2 in methanol

Figure 9 shows the variation of acoustic impedance with an increase in CaF_2 nanoparticles in methanol. It shows similar trends as that of ultrasonic velocity. It is in good agreement with the theoretical requirements. An increase in acoustic impedance shows the association of nanoparticles and a decrease in acoustic impedance shows the dissociation of nanoparticles in nanosuspension.

Figure 10 shows the variation of relaxation time with molar concentration. An increase in relaxation time with an increase in molar concentration of CaF_2 nanoparticles in methanol indicates the stability of CaF_2 nanoparticles in methanol.

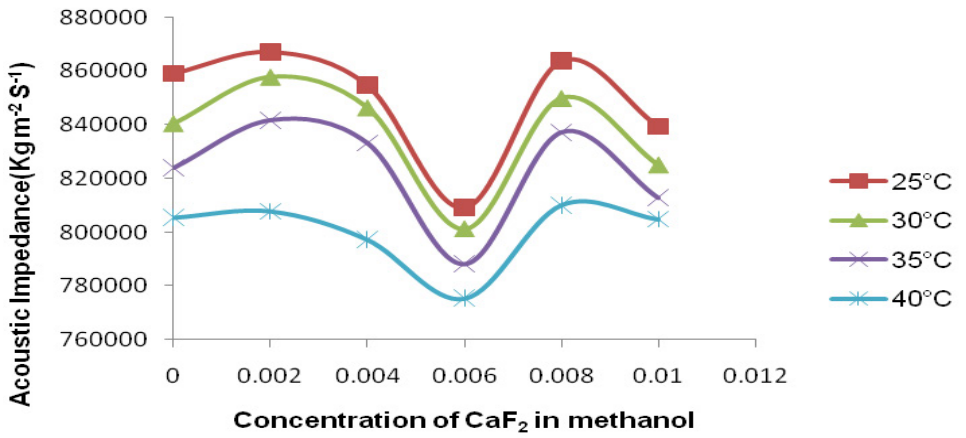

Figure 9. Variation of acoustic impedance with concentration of CaF_2 in methanol

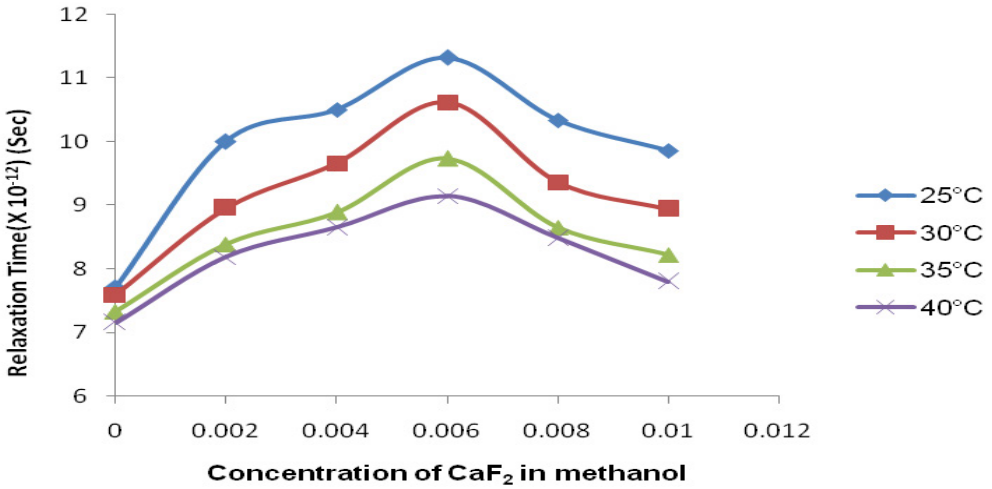

Figure 10. Variation of relaxation time with concentration of CaF_2 in methanol

CONCLUSION

In this study methanol-based, nanosuspension with CaF_2 nanoparticles is prepared by chemical route. The particle size, ultrasonic velocity, density, adiabatic compressibility, isothermal compressibility, free volume, free length, acoustic impedance, and relaxation time of methanol-based nano suspension are measured. The ultrasonic velocity increases with an increase in the concentration of nanoparticles and the enhancement are observed to be 1141.654 m/s and 1100 m/s for the concentration of 0.002 wt/vol% and 0.008 wt/vol% of CaF_2 methanol-based nano suspension respectively. It is due to the association of CaF_2 nanoparticles in methanol-based nano suspension indicating a strong interaction between the constituents. It is observed that ultrasonic velocity decreases with an increase in temperature, this is due to the Brownian motion of nanoparticles in methanol-based nanosuspension and thermal agitation.

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