

On aqueous Fe_3O_4 nanofluid room temperature synthesis and physical properties

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Nanofluids are suspensions of nano to micrometer sized particles in liquids. A simple recipe of preparing small quantity of magnetite nanoparticles in aqueous suspension at room temperature is presented. Physical parameters like conductivity, surface tension coefficient and light scattering parameter were measured and results are presented.

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1. Introduction

The nanofluid notion is a relatively new concept and was first mentioned by Choi in 1995 [1] as he noticed that a small amount of nanoparticles, added in a fluid, considerably enhanced the heat transfer properties [2].

The nanoparticles have a continuous, irregular motion in nanofluids, which is the effect of several factors such as gravity, Brownian force, Archimede's force and friction force between fluid and the particles. The irregular nanoparticle motion in the fluid is the cause the remarkable enhancement of heat transfer properties of the nanofluids [3-6]. When liquid undergoes a change in phase due to the absorption of heat a higher transfer rate occurs. The more efficient heat transfer from the heated surface in the form of heat of vaporization and the bubble-driven turbulence and convection leads to rapid mixing of the fluid and consequently increases the heat transfer properties of the fluid. Therefore, boiling heat transfer has played an important role in industrial heat transfer processes such as macroscopic heat transfer exchangers in nuclear and fossil power plants, and in microscopic heat transfer devices such as microchannels for cooling electronic chips.

The use of boiling is limited by a condition called critical heat flux (CHF). Consequently, the occurrence of CHF is accompanied by an inordinate increase in the surface temperature for a surface-heat-flux-controlled system. Adding solid nanoparticles to common fluids such as water is an effective way to increase the CHF [7]. Materials used for nanoparticles include noble metals (e.g., gold, silver, platinum) and metal oxides (e.g., alumina, zirconia, silica, titania). Previous studies of CHF in nanofluids [8-13] have established that significant CHF enhancement (up to 200%) occurs with various nanoparticle materials, e.g., silicon, aluminum and titanium oxides. They also reveal that such enhancement occurs at low nanoparticle concentrations, typically less than 1% by volume. In theory, nanofluids can improve the

thermal performance of any engineering system that is limited by CHF [7].

The fluid parameters that are relevant to two-phase heat transfer are the boiling point, the surface tension, the thermal conductivity and the viscosity.

In this work a simple recipe to prepare small amounts of magnetite nanofluid at room temperature is presented. The electric conductivity of diluted nanofluid and the surface tension were measured and the results are presented further on. Finally a light scattering experiment was conducted and the light scattering parameter was measured and the results are discussed in connection with nanoparticles aggregates formation in diluted aqueous suspensions.

2. Synthesis of the aqueous nanofluid

The procedure we used to prepare the nanofluid does not require any special equipment and was carried on at room temperature, which was 22 °C. The reagents used were: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, ammonium hydroxide ($\text{NH}_3[\text{aq}]$) 25%, citric acid ($\text{C}_6\text{H}_8\text{O}_7$), all produced by Merck, Darmstadt. All chemicals used were p.a. grade.

The solutions were prepared just before the determinations, in order to prevent their contamination with the atmospheric oxygen. The concentrations were 1M for FeCl_3 , 2M for FeCl_2 , 0.5 M for ammonium hydroxide and 25% for citric acid.

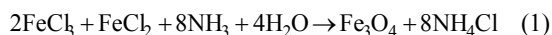
4mL of the 1M FeCl_3 solution and 1 mL of the 2M FeCl_2 solution were poured into a 150 mL beaker. While continuously swirling the iron chloride solution, 50 mL of the 0.5 M ammonium hydroxide were slowly added, dropwise, in such a way that the process lasted for 5 minutes. A black precipitate formed during the slow addition, the precipitate being magnetite ($\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$). A bar magnet was placed under the beaker. It pulled all of the magnetite out of the solution, and the water become

clear. Keeping the magnet on the bottom of the beaker, the excess water was decanted.

The magnetite was rinsed three times by adding deionised water, using the magnet to settle the magnetite, and discarding the clear water, to completely remove the excess ammonium hydroxide from the particles. A certain amount of water was removed to form a viscous fluid.

At this stage of the synthesis procedure the nanofluid, which in this case is a ferrofluid, must be stabilized. This was accomplished by adding 1 mL of the 25% citric acid and mixing the ferrofluid for 2 minutes by moving the beaker over the magnet.

The chemical reaction is:



The output was a viscous, dark brown fluid having the volume ratio of 33%.

The next sections present the results of an attempt to characterize the nanoparticle size by an unconventional light scattering experiment and by conductivity and surface tension measurements.

3. Coherent light scattering experiments

Dynamic light scattering (DLS) is a well established technique for measuring particle size over a size range from nanometers to microns. The particles act like scattering centers in suspension and have a permanent Brownian motion. When the suspension containing nanoparticles is subject to a coherent light beam, an un-uniformly illuminated image is obtained, currently named speckled image, having a statistical distribution of the intensity over the interference field. The speckled image can be observed either in free space and is named objective speckle or on the image plane of a diffuse object illuminated by a coherent source; it is named subjective speckle in [14]. The review paper [15] names the two types of speckled images as far field speckle and image speckle. By placing a detector at a certain angle and recording the scattered light intensity a time series is recorded. As proved in [14], [16], [17] the width of the autocorrelation function of the time series is proportional to the diffusion coefficient, which, on its turn, depends of the particle diameter. This leads to a fast procedure for measuring the particle diameter. The method, which is implemented in commercially available devices, uses the correlation of the Brownian motion with the fluctuations of the far field. As the Brownian motion is connected to the diffusion coefficient, the diameter that is measured is the hydrodynamic diameter, which is different of the physical diameter.

An alternative to the DLS that we suggest in this article is based on measuring the light scattering parameter $g = \langle \cos\theta \rangle$. Basically the far field is recorded using a CMOS with the pixel diameter measured precisely. A movie is recorded and the profile: light intensity versus scattering angle is extracted. The profile is averaged over a big number of frames, to compensate the “boiling speckle” aspect [18]. The experimental setup and details on data processing are presented in [18].

The Henyey–Greenstein phase function (1) is the most commonly used function to describe light scattering anisotropy [19], [20].

$$f(\mu) = \frac{1}{2} \frac{1 - g^2}{(1 - 2\mu g + g^2)^{3/2}} \quad (2)$$

In (1) $\mu = \cos(\theta)$, θ is the polar scattering angle and $g = \langle \mu \rangle$ is the scattering anisotropy parameter. By fitting the integral of the Henyey–Greenstein phase function (1), as explained in [18], on the intensity profile the light scattering parameter g is assessed.

As the nanofluid is optically opaque, it must be diluted for transmission light scattering experiment. In the work described here the volume ratio was 0.05%. Fig. 1 presents the results of the fit performed on the profile that resulted from averaging the first seven minutes after dilution.

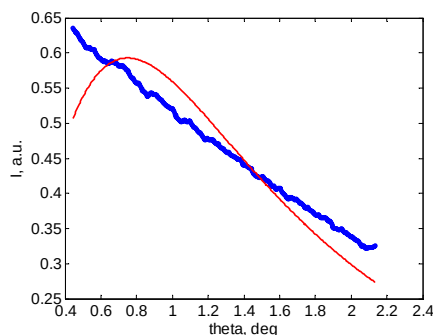


Fig. 1. The scattered light variation with the scattering angle, averaged on the first seven minutes. The thick line is the experimental data and the smooth, thin line is the result of the fit.

The best fit was for $g=0.98163$. The results of Mie scattering calculation [21] and [22] reveal a strong variation of the scattering parameter g with the particle diameter, especially in the small diameters range, as presented in Fig. 2. Data in Fig. 2 is calculated using [21].

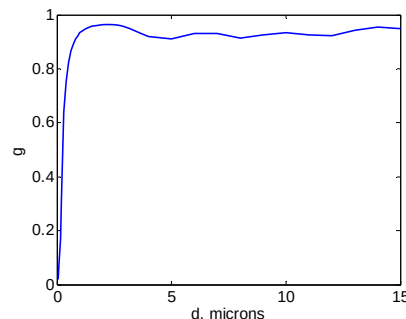


Fig. 2. The variation of the scattering anisotropy parameter g for magnetite spherical particles in aqueous suspension with the nanoparticle diameter.

From Fig. 2 we notice that the $g=0.98163$ corresponds to particles having a diameter around 2 microns. The advantage of this method is that it measures the physical

diameter, as it uses time averages, rather than the hydrodynamic diameter, which is the output of DLS. The disadvantage lays in the fact that the intensity of the light scattered by one nanoparticle is proportional to the six-th power of the diameter. Once big particles appear in suspensions, e.g. nanoparticle aggregates which form fast in aqueous solution, the scattering landscape becomes dominated by them. Consequently this technique does not provide information on the nanoparticles size distribution. Details on this technique are presented in [18] where it was used in an attempt to monitor aggregate formation rate in citric acid coated magnetite nanoparticles in diluted aqueous solution.

The results of the light scattering experiment presented in this work reveal that in the first seven minutes after dilution nanoparticle aggregates with a diameter of 2 microns and bigger are present in suspension in a big concentration. The concentration can not be measured using this technique but is big for making the light scattered by smaller particles to appear as a distortion of the profile in Fig. 1 from the ideal profile corresponding to that particular value $g=0.98163$, the smooth curve in Fig. 1.

4. Electrical conductivity

The electric conductivity of a nanofluid is one of the physical parameters that can play an important role in nanofluids biomedical applications [23]. Electrically conductive nanoparticle suspension is very attractive for tissue engineering because of its potential to modulate cellular activities through electrical stimulation [24], therefore the variation of the electrical conductivity with the nanofluid concentration in aqueous suspension was investigated.

Different dilutions were got from the same concentrated nanofluid described in section 1, having the volume ration 33%. The electrical conductivity of each sample was measured using an OAKTON CON digital conductometer. The results of the electrical conductivity data measured over the coated nanoparticle volume concentration range 0 – 0.016 are presented in Table 1 and in Fig. 3.

Table 1. Electrical conductivity of diluted Fe₃O₄ nanofluid.

Nanopart. vol.ratio, %	Electrical conductivity, $\mu\text{S/m}$
0.00	5.50
0.07	11.90
0.20	29.90
0.26	39.70
0.33	45.40
0.41	55.20
0.49	62.50
0.81	105.50
1.20	144.70
1.59	182.70

The variation appears to be linear in Fig. 3. In order to verify the linear dependence the first degree polynomial coefficients were calculated by the least square method.

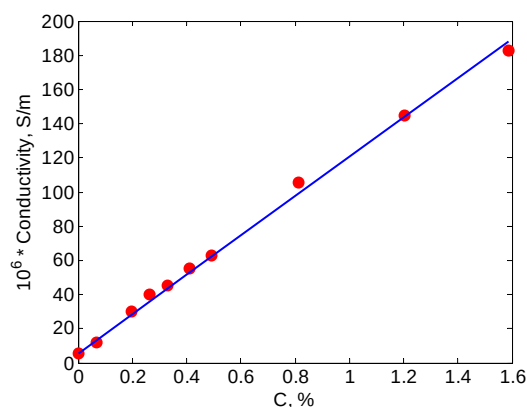


Fig. 3. The variation of the electrical conductivity with the nanoparticle volume ratio. The dots are the experimental data and the line is a linear plot.

Equation (3) describes the variation of the conductivity with the nanoparticle volume ratio. The correlation coefficient is $R^2=0.9968$, which is very close to 1 (perfect fit), meaning that the degree one polynomial describes accurately the variation.

$$\sigma = 115.11 \cdot C + 5.5 \quad (3)$$

In (3) C is the volume ratio and the electrical conductivity σ is expressed in $\mu\text{S/m}$. Examining Table 1 and Fig. 3 we notice a fast increase of the electrical conductivity with the volume ratio and this might be useful in measuring very small amounts of nanoparticles in diluted suspensions. We notice that when the nanoparticle volume ratio increased from 0 to 0.07%, which is 700 ppm, the conductivity increased more than 100%, from 5.5 $\mu\text{S/m}$, which is the deionised water electrical conductivity to 11.90 $\mu\text{S/m}$. This is a large variation that can be easily measured.

5. Surface tension

The surface tension and the contact angle are the two main parameters that affect the wettability of a surface. Surface wettability is the key parameter in heat transfer between a solid surface and a liquid, as pointed out in [7], [25]. For this reason the variation of the surface tension coefficient of the diluted Fe₃O₄ nanofluid in aqueous suspension was investigated. The surface tension coefficient of the diluted nanofluid against air was measured using a stalagmometer. This is a relative method and deionised water at 20°C was considered to be a referential. Special care was taken that both the reference and the samples have the same temperature and this was accomplished by preparing the samples and maintaining them for a five hours at room temperature, which was adjusted to 20°C and measured with a digital thermometer.

The variation of the surface tension coefficient with the nanoparticle volume ratio is presented in Fig. 4. Examining Fig. 4 we notice a decrease of the surface tension coefficient with the increase of the nanoparticle volume ratio. A linear plot on the data is presented in Fig. 4 as well. The stalagmometric method, in the configuration we used had a precision of 1.5%. The data at 0 volume ratio has no error bar as it is considered to be reference.

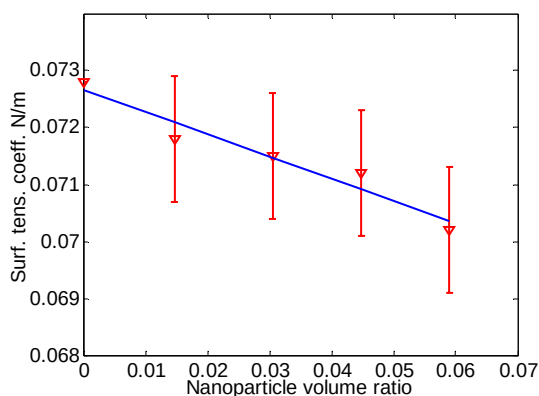


Fig. 4. The variation of the surface tension coefficient with the nanoparticle volume ratio, triangles and the linear fit, solid line.

The linear regression equation is:

$$\sigma_a = -0.0391 \times C + 0.0727 \quad (4)$$

where σ_a is the surface tension coefficient against air, in N/m and C is the nanoparticle volume ratio. The correlation coefficient is $R^2 = 0.9317$, which expresses a good fit, considering the relatively big errors.

The decrease of the surface tension coefficient with the increase of the nanoparticle concentration is in good agreement with the literature. In [25] Alumina nano-fluids were prepared by dispersing alumina nano-particles into pure water; Tri-sodium phosphate (TSP, Na_3PO_4) surfactant was added into the pure water. The results of the surface tension measurements show the same decreasing trend with increasing concentration as [25].

6. Conclusions

In this work a simple recipe to prepare small amounts of Fe_3O_4 nanofluid at room temperature having citric acid as surfactant is presented. Following it a small amount of nanofluid was prepared. An alternative to the typical DLS technique to characterize the nanoparticle size is presented. The shortcoming of the method is that once big clusters are present, they dominate the landscape and the information is not accurate. Nevertheless, using it we found that in a matter of minutes after the dilution micrometer sized clusters are formed in the aqueous suspension.

Conductivity measurements were conducted as well and we found a very fast increase of the conductivity with the increase of the nanoparticles volume ratio and this fast variation can be used to measure very small concentration, in the range 0 – 16000 ppm.

The surface tension of the diluted nanofluid against air was measured as well. We found a decrease in the surface tension coefficient with the increase of the nanoparticles concentration, in good agreement with the literature.

Further work is scheduled to improve the precision of the experimental work.

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