Electrostatically Stabilized Nanofluid Preparation by Chemical Co-Precipitation and the Effect of Particle Size on Nanofluid Viscosity

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ABSTRACT
In this study, electrostatically stabilized nanofluids with different particle sizes were prepared by chemical co-precipitation with double-sided titration process, and the effect of particle size on nanofluid viscosity was investigated and analyzed. Conditions of temperature, pH value, and acidic aqueous solution molarity during the experiments were adjusted to obtain electrostatically stabilized Fe₃O₄ nanoparticles of different sizes. The viscosity of fluids containing suspended nanoparticles was then measured at different temperatures to determine the effect of particle size. The results showed that an increase in the temperature of the co-precipitation environment caused an increase in particle size. However, an increase in the pH value caused a reduction in particle size. The particle size obtained with lower molarities of acidic aqueous solution was smaller than that obtained with higher molarities. The viscosity of electrostatically stabilized nanofluids with smaller particles was found to be higher than that of fluids with larger particles in fluids with the same concentration of particles.

KEYWORDS
Ferrofluids; chemical co-precipitation; nanoparticle size; viscosity

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1. Introduction

The rapid advance of technology has resulted in demand for all kinds of specialized material, including smart material. Smart material with nano-structure is simply called smart nanomaterial. One of the most intensively discussed nanomaterials is the fluids containing nanoparticles, the so-called nanofluids. The first application of nanofluids was in 1965, when a NASA researcher Papell [1,2] used ball milling on magnetite ($Fe_3O_4$) to produce nanoparticles. These were suspended in kerosene and oleic acid was used to coat the particles and stabilize suspension. This nanofluid was used in space sealing systems. Subsequently, Shimoizaka [3] used chemical co-precipitation to successfully produce nanoparticles, this is not only faster than ball milling, but also less expensive. Shimoizaka et al. [4] then used this method to prepare nanofluids.

In the 1980s, Massart [5] used water as the carrier liquid to prepare nanofluids that have different fluid properties than oil-based ones. Shao [6] collated numerous methods for stabilizing nanoparticles in a carrier liquid [7]. One method used a surface electrostatic charge and colloidal stability theory established by Derjaguin, Landau, Verwey, and Overbeek in the 1940s [8,9], also known as the DLVO theory. This theory asserts that while particles are attracted to one another, the electrical double layer between the particles and the carrier liquid also causes electrostatic repulsion and particle stability depends on a balance between attraction and repulsion. Should attraction be greater than repulsion, stability is poor and particles rapidly cluster and precipitate. Conversely, when repulsion is greater than attraction, the nanofluids will be stable. We call this type of stability electrostatic stabilization. The method that uses coated particles to stabilize the fluid is called steric stabilization. Electrostatic stabilization can be more rapidly achieved and the suspension is not affected by the amount of stabilizer. The concept of the electrical double layer was first proposed by Helmholtz [10], who simulated the outer structure of particles to describe how they affect ions in the carrier liquid causing them to cluster around the particle. This produces an electrified ion diffusion layer and causes uneven electric charge distribution. In recent years, many studies have used electrostatically stabilized nanofluids to conduct experiments. Chen et al. [11] used electrostatically stabilized nanofluids to carry drugs. They compared the use of medicated fluid (by guiding the fluid to treat the affected area) with and without an added magnetic field and successfully increased drug suppression of cancer cell growth using a magnetic field. Srinivas et al. [12] experimented with electrostatically stabilized nanofluids and found that adding nanofluids to heat exchangers can enhance heat transfer.

The ease with which nanofluids could be produced became the focus of many investigations, as well as particle size and its correlation to nanofluid characteristics. Chon et al. [13] dripped nanofluids with particles of different size onto a flat surface which was then heated until the drops evaporated. They found that the residual particles left different characteristic tracks after evaporation. Lee et al. [14] showed that the thermal conductivity of nanofluids increased with a decrease in particle size. These experiments all showed that particle size is significantly correlated with nanofluid characteristics. However, controlling particle size in a manufacturing process is quite another topic. Chia et al. [15] introduced the chemical co-precipitation method and indicated that low temperature and high stirring speed can produce smaller sized particles. They also stated that control of average size could be achieved by careful adjustment of the pH value.

Today, nanofluids are being applied to the solution of many fluid dynamic problems. However, most of the nanofluids used in previous work have different particle sizes and it is easy to theorize that particle size has an effect on fluidity. In this study, we explored a method for the production of nanofluids with different particle sizes, and we also explored the effect of particle size on the nanofluid viscosity. In addition, we carried out a literature survey and found that during the chemical co-precipitation manufacture of nanoparticles, the environment pH value changes. We made this an important point in our study and proposed a novel process using double-sided titration that prevented the change of pH value in the process of co-precipitation to obtain electrostatically stabilized $Fe_3O_4$ nanoparticles of different sizes. A second point for investigation was the determination of the viscosity of electrostatically stabilized nanofluids with different particle sizes at different temperatures.

2. Research Method

2.1. Double-sided Titration Experiment

In this study, we used double-sided titration to maintain a stable pH value in the process of co-precipitation.

2.1.1. pH Value Calculation

Before describing double-sided titration, we must first explain the pH formula, as shown below:

$$[H^+][OH^-] = 1 \times 10^{-14} M^2 \quad (1)$$

$$\text{pH} = -\log[H^+] \quad (2)$$

The definition of pH value is based on the fact that at standard temperature and pressure, the product of naturally ionized hydrogen ion molarity and hydroxide ion...
molarity is always $10^{-14}$ M. To obtain the pH value of a liquid, Equation (1) must first be used to obtain the [H$^+$] molarity, then the [H$^+$] molarity must be substituted into Equation (2) to obtain the pH value. It should be noted that the range of pH values is between −1 and 15, with −1 being the value for a 10 M solution of HCl and 15 being the value for a solution of 10 M NaOH [16].

### 2.1.2. Double-sided Titration

In the traditional method used for the chemical co-precipitation manufacture of nanoparticles, FeCl$_2$ and FeCl$_3$ are first dissolved in water, then the two aqueous solutions are mixed in acidic conditions. The acidic aqueous solution is then titrated against an NaOH alkaline aqueous solution so that a co-precipitation reaction is started. The reaction produces Fe$_3$O$_4$ nanoparticles. This titration process causes the environment pH value to change continuously. For this study, an additional titration was performed with a NaOH+DI water alkaline aqueous solution, as shown in Figure 1. By adding NaOH, we were able to control the pH value of the co-precipitation environment (CE) in a reaction vessel, so as to prevent the change of pH value. The acidic aqueous solution was titrated at a fixed flow rate ($2.143 \times 10^{-5}$ kg/s) into a CE alkaline aqueous solution. At the same time, NaOH alkaline aqueous solution was titrated at the same flow rate into the co-precipitation solution. The solution was stirred while being titrated at 1000 rpm to ensure an even distribution of the reaction fluids and maintain the CE pH value. In addition, a constant temperature water bath was used to control the CE temperature. Different amounts of FeCl$_2$ and FeCl$_3$ were used to change the molarity of the acidic aqueous solution.

### 2.2. Electrostatically Stabilized Fluid Preparation

After chemical co-precipitation, electrostatic stabilization was used to stabilize the suspension.

#### 2.2.1. Chemical Co-precipitation Method

Shimoizaka [3] first used chemical co-precipitation to prepare nanoparticles in 1966. Since then, chemical

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**Figure 1.** Double-sided chemical co-precipitation titration.

**Table 1.** Chemical co-precipitation environment temperature parameters.

| Process No. | FeCl$_2$ (g) | FeCl$_3$ (g) | NaOH (g) | CE NaOH (g) | CE temperature (°C) |
|-------------|--------------|--------------|----------|-------------|---------------------|
| #1          | 1.243        | 2.028        | 42       | 10          | 10                  |
| #2          | 1.243        | 2.028        | 42       | 10          | 20                  |
| #3          | 1.243        | 2.028        | 42       | 10          | 30                  |
| #4          | 1.243        | 2.028        | 42       | 10          | 40                  |
| #5          | 1.243        | 2.028        | 42       | 10          | 50                  |
| Di water    | +25 ml       | +25 ml       | +50 ml   | +25 ml      | –                   |
| +50 ml      |              |              |          |             |                     |
co-precipitation has become the mainstream method for producing nanoparticles. The co-precipitation Fe$_3$O$_4$ nanoparticle chemical reaction used in this study was as follows:

$$\text{FeCl}_3 \cdot 4\text{H}_2\text{O} + 2\text{FeCl}_2 + 8\text{NaOH} \rightarrow \text{Fe}_3\text{O}_4 + 8\text{H}_2\text{O} + 8\text{NaCl} \quad (3)$$

An electronic balance was used to weigh the appropriate amounts of iron(II) chloride tetrahydrate (FeCl$_3$), iron(III) chloride (FeCl$_2$), and NaOH which were all dissolved in a set amount of deionized (DI) water. Iron(II) chloride acidic aqueous solution, iron(III) chloride acidic aqueous solution, and NaOH solutions were prepared. The acidic aqueous solution obtained by mixing FeCl$_3$ and FeCl$_2$ and the alkaline aqueous solution were simultaneously titrated into the reaction vessel and rapid stirring ensured good mixing and proper co-precipitation. The quantities of chemicals used are shown in Tables 1–3. For example, in Process #10, 4.97 g of FeCl$_3$, 8.11 g of FeCl$_2$, 48 g of NaOH, and 10 g of CE NaOH were completely dissolved with stirring in 25, 25, 50, and 25 ml of deionized water. The parameters for Process #10 were 0.5 M FeCl$_3$ aqueous solution and 1 M FeCl$_2$ aqueous solution. According to Equation (3), 4 M of NaOH in the reaction vessel was used to produce chemical products. The additional NaOH titration can be used to supply the amount consumed, which also allows the co-precipitation environment to remain at a molarity of 10 M before and after the chemical reaction. Due to the co-precipitation environment being 10 M NaOH aqueous solution, a pH value of 15 was calculated using Equations (1) and (2).

### 2.2.2. Electrostatic Stabilization

Because nanoparticles can easily aggregate in aqueous solution, the particles need to be stabilized. The most common stabilizing methods include electrostatic stabilization and steric stabilization. Electrostatic stabilization was utilized in this study. This method is based on the special characteristic that electrons move freely in metals so that ion clusters with opposite charge will arrange themselves close to the solid metal surface in a tight array, called the Stern layer. Outside the Stern layer, there is another layer more loosely arranged and less compact, called the diffuse layer. The Stern layer and the diffuse layer form the electrical double layer. A stable suspension will be achieved when the attraction between particles is weaker than the repulsion of the electrical double layer particles.

An ultrasonic processor was used in this study to agitate the OH– ions, present in high molarity, to make them adhere to the surfaces of the suspended particles. This produced an effective electrical double layer of ions to stabilize the suspension.

### 2.3. Measuring Particle Size and Nanofluid Viscosity

In this study, we used dynamic light scattering (DLS) for particle size analysis. This technique employs a beam of laser light which is directed into the solution. Small particles suspended in fluid will scatter the laser light and the degree of scattering is related to the brownian motion of the particles and therefore also closely related to particle size. The changes in this scattered light over time is measured and used to calculate particle size distribution. However, if the particle concentration of the test solution is high, the scattered light from a single particle will be scattered again by other particles. This makes it necessary to dilute the nanofluid enough so that the amount of scattering gives a true approximation of particle size. In this study, all nanofluids were diluted with the same pH NaOH aqueous solution at a ratio of 1:200 and then measured the particle size distribution of nanoparticles in fluids by DLS. The average nanoparticle diameters for different process conditions were then obtained as follows: #1, 34.37 nm; #2, 47.16 nm; #3, 63.60 nm; #4, 78.01 nm; #5, 98.07 nm; #6, 138.49 nm; #7, 121.19 nm; #8, 106.32 nm; #9, 75.75 nm; #10, 53.48 nm; #11, 34.37 nm; #12, 38.29 nm; #13, 44.43 nm; and #14, 53.48 nm.

To investigate the effect of particle size on the nanofluid viscosity, in addition to the particle size, the fluid conditions (including the particle volume fraction and carrier liquid pH value) must be the same. The viscosity measurements can then be proper. NaOH was dissolved in DI water to prepare a carrier liquid with a pH value of 15, and nanoparticles were then dispersed in the carrier liquid using an ultrasonic processor, so as to obtain
electrostatically stabilized nanofluids with a particle volume fraction of 0.22%. A rotational viscometer was used to measure the viscosity of the prepared nanofluids. This device measures the shear force exerted by the fluid against a turning cylinder. The torque and turning speed of the cylinder are measured and can be used to calculate the nanofluid viscosity. A constant temperature water bath was used to control the temperature of the working fluid. The calculated data of nanofluid viscosity from the measurements were compared with theoretical values. Previous studies [17,18] showed that the viscosity of nanofluids considering the roles of particle concentration and particle interaction is determined by the following relationship:

$$\mu = \mu_f (1 - \varphi)^{-\varepsilon/2}$$  \hspace{1cm} (4)

In which, $\mu_f$ is the carrier liquid viscosity, $\varphi$ is the particle volume fraction, and $\varepsilon$ is the viscosity corrective factor due to particle interaction. When there is no force between the particles or particles and the surface, $\varepsilon = 1$. $\mu_f$ was set as the viscosity of NaOH aqueous solution that has a pH value of 15. The experimental data were compared with the theoretical results at different temperatures.

### 3. Results and Discussion

The influences of temperature, pH value, and acidic aqueous solution molarity on particle size were analyzed, respectively. The viscosity of prepared nanofluids with different particle sizes was measured at different temperatures to determine the effect of particle size.

#### 3.1. Effect of Environment Temperature on Particle Size

Figure 2 shows the average nanoparticle diameter $d$ obtained between the environment temperature $T = 10$ and $50$ °C at an environment pH value of 15 and an acidic aqueous solution molarity of 0.75 M. Results show that the particle size increase is virtually linear as the co-precipitation environment temperature rises. The particle size goes from 34.37 nm at 10 °C to 98.07 nm at 50 °C, representing an increase of about 185.34%. This increase is probably due to the effect of temperature on the co-precipitation particle synthesis reaction rate. The higher the temperature, the faster the reaction rate will be. If the reaction rate is faster, the co-precipitation particles have become larger as the electric double layer forms a barrier on the particle surface. The accelerated reaction rate at high temperatures may, therefore, be the main cause of increased particle size.

#### 3.2. Effect of Environment pH Value on Particle Size

Figure 3 shows the average nanoparticle diameter $d$ obtained between the environment pH value $pH = 13$ and 15 at an environment temperature of 10 °C and an acidic aqueous solution molarity of 3 M. Results show that as the pH value rises, the particle size shows a nearly linear decrease, dropping from 138.49 nm at $pH = 13$ to 53.48 nm at $pH = 15$. This is a 61.38% decrease in particle size. The main reason for this decrease may be because an effective electrical double layer was assembled during the reaction. The greater abundance of OH$^-$ ions in

![Figure 2. Relationship between particle size and co-precipitation environment temperature.](image)
the environment at a higher pH allows a faster assembly of repellant electrical double layers around the particles. The nanoparticles are better segregated, and the smaller ones are produced. The increased OH\textsuperscript{-} ion concentration at high pH values may, therefore, be the main cause of decreased particle size.

### 3.3. Effect of Acidic Aqueous Solution Molarity on Particle Size

Figure 4 shows the average nanoparticle diameter $d$ obtained between the acidic aqueous solution molarity $M = 0.75$ and $3 \text{ M}$ at an environment temperature of $10 \, ^\circ\text{C}$ and an environment pH value of 15. The figure shows that as the acidic aqueous solution molarity increases, the particle size tends to increase dramatically. The particle size went up from $34.37 \, \text{nm}$ at $0.75 \, \text{M}$ to $53.48 \, \text{nm}$ at $3 \, \text{M}$. This is an increase of $55.60\%$ and may be related to the proximity of reactants. A more dilute acidic solution has fewer reactants than the more concentrated acidic solution and when the co-precipitation reaction is initiated less product is obtained due to the more separated reactants. If the acidic solution is more concentrated, the co-precipitation particles have become larger as the electric double
layer forms a barrier on the particle surface. The proximity of reactants at high molarities of acidic aqueous solution may, therefore, be the main reason for the increase in particle size.

3.4. Effect of Particle Size on Nanofluid Viscosity

The viscosity of nanofluids with a particle volume fraction of 0.22% and a pH value of 15 at five different particle sizes was measured at different temperatures. Figure 5 shows the variation of the nanofluid viscosity $\mu$ with the average nanoparticle diameter $d$ at 10, 30, and 50 °C. The figure shows that the viscosity of a nanofluid with larger particles is close to the theoretical value. This is especially true at the lower temperatures. As particle size decreases, the nanofluid viscosity increases. Although an increase in temperature causes a drop in nanofluid viscosity, it does not seem to cause a significant rise or fall in the variation of $\mu$ with $d$. It should be noted that previous studies showed that the particle size and the viscosity are not directly related, and only correlate to the carrier liquid and particle volume fraction; however, the results of this study showed that when particles are at the nanoscale (down to 100 nm), the viscosity of nanofluids could increase with a decrease in particle size. The reason for the enhanced viscosity may be due to large specific surface area (total surface area per unit of mass) that provides high stabilization against particle sedimentation and significantly increases the collision and friction between particles.

4. Conclusions

In this study, the effects of temperature, pH value, and acidic aqueous solution molarity on particle size resulting from chemical co-precipitation with double-sided titration process based on electrostatic stabilization, as well as the effect of particle size on nanofluid viscosity, have been investigated and analyzed. The temperature of the co-precipitation environment was controlled by the use of a constant temperature water bath, the pH value of the co-precipitation environment was controlled by the addition of NaOH, and the molarity of the acidic aqueous solution was changed by the addition of FeCl$_2$ and FeCl$_3$. DLS was used for particle size determination, and a rotational viscometer was used for nanofluid viscosity determination at different temperatures.

The research findings obtained are given as follows:

1. At the higher environment temperatures used, co-precipitation nanoparticles sizes are larger, and particle size increases in an almost linear fashion with an increase in temperature.
2. Nanoparticles produced through chemical co-precipitation in a higher environment pH value are smaller. Particle size decreases in an almost linear fashion with an increase in pH value.
3. Co-precipitation in an acidic solution of lower molarity produces smaller nanoparticles. Particle size dramatically increases with an increase in the molarity of the acidic solution.
(4) In the 10–50 °C temperature range, the smaller the particle size, the higher the nanofluid viscosity; however, temperature had no significant impact on the particle size effect.

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