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A Combined Method for Synthesis of Stable Ferrofluids

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Abstract:

Ferrofluid is a colloidal suspension of single domain ferromagnetic nanoparticles dispersed in a carrier fluid. Ferrofluids have been an interesting matter for scientists in different fields due to their unique characteristics of showing change in their physical properties under the influence of magnetic field. However, they have not been commercialized yet at a great level. The primary reason for this is the lack of stability in ferrofluids against agglomeration and gravitational sedimentation of the magnetic nanoparticles. There are different factors that determine the stability of ferrofluids; some of them are: type and size of the magnetic nanoparticles, type of surfactant, type of carrier fluid, method of coating, etc. There are methods of synthesis those keep some of these factors in consideration, however, there are not many methods in existence those can incorporate all of these factors. To develop a method that can incorporate majority, if not all, of these factors and can provide good stability, we have presented the results of our literature review in this paper by incorporating crucial steps from different methods of synthesis of ferrofluids and suggesting a method as a combination of all these crucial steps required for the synthesis of stable ferrofluids.

Keywords

Ferrofluid, ferromagnetic nanoparticles, surfactant

1. Introduction

Ferrofluid is a colloid suspension of single domain ferromagnetic nanoparticles dispersed in a carrier fluid [1]. The optimum size of the magnetic nanoparticles is reported to be between 10 nm and 20 nm to keep the particles suspended in the carrier fluid through Brownian motion [1-3] and prevent them from settling down due to gravity. Ferrofluids possess the properties of a magnetic solid as well as a fluid partially, thus, the state of the ferrofluid can be altered by varying the magnetic field. The flow properties can also be finely tuned through variation of magnetic field. Therefore, the field of ferrofluids has a scope of diverse applications. There has been research going on to devise various applications of ferrofluids such as doping for technological materials, dynamic sealing, damping, heat dissipation [2], as a working body in tilt sensors [4], improving the efficiency of a PVT (photovoltaic unit) system in a solar cell [5], lubrication [6], and many more. However, they have not been commercialized yet at a great level. The primary reason for this is the lack of stability in ferrofluids against agglomeration and gravitational sedimentation of the magnetic nanoparticles. There are different factors that determine the stability of ferrofluids; some of them are: type and size of the magnetic nanoparticles, type of surfactant, type of carrier fluid, method of coating, etc. The factors have been discussed in detail in the following chapters.

2. Factors for Consideration

2.1. Magnetic Phase

The magnetic phase is the core part of a ferrofluid as it gives it the characteristics to be influenced by magnetic field. Pure metals such as Iron (Fe), Cobalt (Co) and Nickel (Ni) can be the most favourable to constitute the magnetic phase, ideally, as they possess the highest saturation magnetization. However, these metals are highly vulnerable to oxidation and thus magnetic particles such as ferrites like maghemite (γ-Fe_2O_3), magnetite (Fe_3O_4), or ferrites of other metals ($MO.Fe_2O_3$, M is a divalent ion, e.g. Mn, Zn, Ni, Co, etc.) [2]. Magnetite is commonly used in the synthesis of ferrofluids. There are several methods available for the synthesis of magnetic nanoparticles. Laokul et al. have used the sol-gel pyrolysis method to produce nano-sized Fe_2O_3 particles [7]. Thermal reductive decomposition method has been used by Xu et al. [8], and Bica [9]. Waje et al. have performed mechanical alloying to synthesize the nanoparticles [10]. Various scientists have performed the hydrothermal technique for the synthesis of nano-sized ferrite particles [11, 12]. Size reduction using wet milling has also been used as a technique to synthesize ferrite nanoparticles in large quantity [13]. However, the chemical method of co-precipitation (also known as Reimer's co-precipitation method) has been found to be a facile and cost-effective method for the synthesis of magnetic nanoparticles, especially magnetite nanoparticles [1].

In the chemical co-precipitation method, the size, composition and shape of the magnetic nanoparticles can be regulated by varying the ratio of Fe^{3+} and Fe^{2+} ions, ionic strength and pH of the continuous medium used. The optimum size of the nanoparticles has been found to be between 10 nm and 20 nm. Within this range of size, the thermal energy of the nanoparticles is greater than the gravitational energy; therefore the nanoparticles can remain suspended in the carrier medium against the gravitational force, through Brownian motion [1-3]. It is, however, not necessary to have only one size of particles in a ferrofluid. Zubarev and co-workers [15, 16], who first proposed the chain-structure formation of the particles under the influence of magnetic field, regarded the ferrofluid as a polydisperse system consisting of nanoparticles of varying sizes and also proposed that the big particles are responsible for the formation of chain-structure which plays an important role in the change in viscosity of the ferrofluid under the influence of magnetic field.

2.2. Carrier Fluid

The main role of a carrier fluid is to serve as a medium in which the magnetic nanoparticles can be suspended, so that the magnetic particles can also acquire the property to 'flow'. There have been various liquids used as carrier fluids for the ferrofluids. Some of them are: Water, Lubricating oil, Synthetic or semi-synthetic oil, Kerosene, Silicone oil, Mineral oil, and combinations of these [2]. The carrier liquids can have different dielectric properties and hence can be polar or non-polar (organic) liquids. The ferrofluids can be ionic fluids or organic-based fluids respectively, based on the type of carrier fluid chosen. There are various factors that need to be kept in mind while choosing the carrier medium for the synthesis of ferrofluids. Some of them are listed as follows [2]: Dielectric properties, Viscosity, Boiling temperature, Vapour pressure at elevated temperature (Volatility), Freezing point. The carrier fluid should be non-reactive with the magnetic material, surfactant and the material used in the ferrofluidic device.

The choice of a suitable carrier medium also depends on the field of application of ferrofluid. For example, for lubrication, the carrier medium for the ferrofluid should be a lubricant. D. Yu Borin and co-workers [4] have shown that how the choice of carrier fluid affects the properties of a ferrofluid, by using two different carrier fluids to synthesize ferrofluids and comparing them.

2.3. Stability of Ferrofluids

Synthesis of highly stable ferrofluids is still a major concern. The small size of the nanoparticles helps to prevent settling of particles individually, however, there are attractive forces present in a suspension of nanoparticles that force the particles to aggregate and settle down as bigger particles. There are two main types of forces acting on the nanopaticles in a ferrofluid: magnetic dipole-dipole attraction and van der Waal's forces between the particles [2]. These forces tend to make the ferrofluidic suspension unstable.

One way to deal with this problem is to introduce steric repulsion and/or electrostatic repulsive forces between the particles to counteract the attraction of magnetic dipole-dipole and van der Waals interactions. This can be done by coating the magnetic nanoparticles with a layer or a number of layers of surfactants to increase the hydrodynamic diameter and hence reduce the van der Waals and magnetic dipole-dipole attractive forces between the nanoparticles [17].

Stability of a ferrofluid depends on the contribution to thermal energy of the particles and on the equilibrium between the attractive and repulsive interactions. Under the influence of magnetic field, the magnetic energy directs the particles to higher intensity regions while the thermal energy drives the particles to roam around in the carrier fluid. The stability against aggregation of particles is usually high when the ratio of the thermal energy and the magnetic energy is high. The stability against sedimentation because of gravitational force is high when the ratio of the gravitational energy and the magnetic energy is low [2].

Brownian motion, steric repulsion and electrostatic repulsion are the primary mechanisms that favour the stability of ferrofluids. While Brownian motion depends heavily on the size of the magnetic nanoparticles, the steric and electrostatic repulsion mechanisms depend on the properties of the carrier medium and the surfactant used. The dominance of electrostatic repulsion is more in ionic or polar ferrofluids while the dominance of steric repulsion is more in organic-based ferrofluids. For organic-based ferrofluids, only one layer of surfactant is needed to form a hydrophobic layer around the particles while in a polar ferrofluid, multiple layers of surfactant might be needed to make them hydrophilic in nature [2]. It was shown by Huang and Wang [18] that ferrofluids with good stability cannot be prepared without coating the magnetic nanoparticles.

2.4. Surfactant

Surfactants are usually long-chain compounds such as fatty acids that have a polar head and a polar or non-polar tail. The polar head of the surfactant gets attached to the surface of the magnetic nanoparticle while the tail provides a distance between the particles through steric or electrostatic repulsion and also ensures the compatibility of the particles with the medium [2]. The surfactant molecules form micelle around the particles to segregate the particles from each other. The micelle-coated particles need to have a minimum distance between them to prevent them from agglomerating [3]. Therefore, the surfactants have a dual purpose in the synthesis of ferrofluids. Firstly, they prevent agglomeration of the magnetic nanoparticles and secondly, they ensure compatibility of the particles with the carrier fluid.

It is important to choose the surfactant and the number of surfactant layers around the particles based on the dielectric properties of the carrier fluid. If the carrier liquid is non-polar or organic, the particles need a single layer of surfactant around them, while if the carrier liquid is a polar fluid such as water, at least two layers of surfactant are needed [2]. More the number of layers more will be the stability of the ferrofluid. The multiple layers can be prepared using a single surfactant or multiple surfactants. Tongxiao and co-workers [19] had prepared a ferrofluid with a tetra-layer coating. Mixing different surfactants to enhance the stability of ferrofluids is another approach that has been used by D.Xu Borin and co-workers [4]. Polyvinyl alcohol, chitosan, ethylene glycol, silica, etc. can be used in water-based ferrofluids. Tartaric acid and Citric acid can also be used to prepare stable ferrofluids over a large pH range. In some cases, anti-oxidation agents are also added with surfactant to prevent oxidation of the nanoparticles. Oleic acid is one of the most common surfactant used in the synthesis of ferrofluids. More information about these surfactants can be found in the review given by Genc and Derin [2].

3. Synthesis of Ferrofluid

There are a lot of good methods available for the synthesis of ferrofluid. However, a standard method is yet to be identified that can serve as a template for the preparation of any kind of ferrofluid. Most of the methods do not give perfect results as far as the quality and stability of ferrofluid is concerned, although each of these methods showcase some crucial steps involved in the synthesis. In this paper, some of these crucial steps used in different methods have been combined and presented in a single method. These crucial steps can be combined with each other in a single method, because these are more fundamental in nature than empirical. The method presented here is for the synthesis of ferrofluid with paraffin oil as carrier fluid and magnetite as the magnetic phase and is divided into two parts: Synthesis of magnetite nanoparticles, and Coating and suspension of nanoparticles.

3.1. Synthesis of Magnetite Nanoparticles

This method for synthesis of magnetite nanoparticles is also known as Reimer's co-precipitation method [20]. Ferrous chloride tetrahydrate ($FeCl_2.4H_2O$), Ferric chloride hexahydrate ($FeCl_3.6H_2O$), aqueous ammonia ($NH_3.H_2O$) are required. The method is described in steps as follows:

i. Add 10.82 g Ferric chloride hexahydrate and 3.98 g Ferrous chloride tetrahydrate in 100 ml distilled water.

ii. Place the solution in ultrasonic bath to provide ultrasonication as well as heating.

iii. Drop aqueous ammonia in the solution when the temperature reaches to 50 ^{0}C till the pH reaches 9. The chemical reaction is as given below [21]:

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe_3O_4\downarrow + 4H_2O$$

iv. Disperse the suspension with ultrasonic bath at 50 ^{0}C for 30 minutes.

v. Use magnetic decantation to separate the particles from the solution.

vi. Wash the particles with 5% aqueous ammonia solution [20] and then with water 3-4 times.

Here, ultrasonication helps in providing more surface area for the reactant molecules to interact and also to prevent the agglomeration of resulting magnetite nanoparticles.

3.2. Coating and Suspension of Nanoparticles

Magnetite nanoparticles (synthesized in the first part), oleic acid, Paraffin oil (light), Nitric acid (10 % v/v), Acetone are required for this part of synthesis. The method is described in steps as follows:

i. Suspend the magnetite nanoparticles, prepared using co-precipitation method, in 100 ml distilled water.

ii. Stir and disperse the particles and keep in ultrasonic bath at 55 ^{0}C for 5-10 minutes

[19]. This helps to keep the nanoparticles dispersed and prevents agglomeration to allow more surface area for the oleic acid molecules to form micelle.

iii. Drop ammonia solution in the suspension to bring the pH to 10 [19].

iv. Add 8 ml oleic acid to the suspension drop-by-drop. Stir and disperse the suspension using ultrasonic bath at 55 ^{0}C. Aqueous ammonia reacts with oleic acid to form ammonium oleate which gets ionised to ammonium ion (positive ion) and oleate ion (negative ion).

v. After cooling the solution, add a diluted solution of Nitric acid (HNO_3) till pH reaches up to 5. The isoelectric point of magnetite is pH_{iep} = 6.5. At a pH below this, the surface of magnetite is positively charged and the concentration of oleate ions is high enough for the chemisorption of oleate ions on magnetite surface to occur [21].

vi. Locate a magnet at the bottom of the beaker to separate the coated magnetite nanoparticles from the rest of the solution.

vii. Wash the coated particles with distilled water at 30 ^{0}C and with acetone to remove traces of water and non-adsorbed oleic acid [21-22].

viii. Disperse the coated nanoparticles in paraffin oil. Keep the suspension in ultrasonic bath to ensure proper dispersion of particles.

4. Characterization Techniques

It is necessary to characterize the ferrofluid once it is synthesized. Table 1 shows some of the characterization techniques used commonly by researchers in the field of nanotechnology or more specifically in the field of ferrofluids.

Table 1. Characterization Techniques

Technique	**Purpose**
Transmission Electron Microscopy (TEM)	Average diameter of particles; particle morphology [21]
X-ray Diffraction	Analysis of Crystal Structure [21]
Magnetometer	Magnetic Properties of the ferrofluid [21]
Roational Rheometer	Rheology of Ferrofluid [4]

5. Summary

Ferrofluid is an important matter for research as it can lead to various new applications and can also improve some of the existing applications. However, to commercialize a ferrofluid-based technology, it is important that to focus upon improvement of synthesis methods to develop a “template” method that can be used to develop any multiple kinds of stable ferrofluid in a facile and cost-effective manner. Development of a good “template” method can also be helpful in developing stable ferrofluids compatible with different kinds of applications, just by modifying some of the steps of the template according to the area of application. The method suggested in this paper is also a sort of template method that identifies various crucial steps involved in the preparation of any kind of stable ferrofluid. The method is, however, subject to be experimented and improved and is majorly based on the fundamental reasoning. Hence, an improvement in the existing method is always possible and would help in the development of a standard or template method.

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