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Synthesis of Ferrofluid and Its Applications - A Review

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ABSTRACT

A ferrofluid is a liquid which becomes highly magnetized in the presence of a magnetic field. The most common materials used in making these magnetic particles are iron oxides such as magnetite (Fe3O4) and hematite (Fe2O3), though other ferromagnetic or ferrimagnetic substances can be used. The particles are usually less than 10nm across. Once a magnetic field is applied to a ferrofluid, the nanoparticles are attracted and pull the entire liquid towards the magnetic field. However, if exposed to a strong magnetic force, some of the nanoparticles can be ripped out from the carrier fluid, forming an incredibly fine dust. Ferrofluids can have very high thermal conductivities and their heat transfer properties are exploited in devices such as loud speakers where they are used to cool the voice coil. Ferrofluids are also the focus of current scientific research and have the potential to be used in many medical applications. In magnetic drug targeting for example, where drugs could be enclosed by ferrofluid and, once injected into the specific body area requiring treatment, a magnetic field could be applied to keep the drugs in this target area. This review paper focus on the synthesis of ferrofluid and these applications in various fields like biomedical, optics, electronics, heat transfer and mechanical engineering.

Keywords: Ferrofluid, Magnetic Fluid, Nanoparticle.

1. INTRODUCTION

A ferrofluid is a liquid that becomes strongly magnetized in the presence of a magnetic field. NASA first developed ferrofluids in the 1960's whilst researching methods of using liquids in space, but in the 21st century ferrofluid has found new levels of fame.They are incorporated into the voice coil gap of loudspeakers for damping undesired vibrations and for cooling. These particles commonly have diameters between 5 and 20 nm, and are composed of a magnetic material such as maghemite (γ – Fe2O3), magnetite (FeO.Fe2O3) or cobalt ferrite (CoO.Fe2O3).The nanoparticles undergo translational and rotational Brownian motion, and are kept suspended in the carrier fluid by either an electric double layer or a surfactant/polymer coating preventing particle agglomeration (I.Torres-D et al., 2014). Ferrofluids have also been used in the separation of metals from ores by taking advantage of a density change that appears in the fluid under application of a magnetic field. One South African company has even been utilizing ferrofluids to separate diamonds from beach sand (Ogden.F, 1993).The name ferrofluid was introduced, the process improved, more highly magnetic liquids synthesized, additional carrier liquids discovered, and the physical chemistry elucidated by R. E. Rosensweig and colleagues; in addition Rosensweig evolved a new branch of fluid mechanics termed ferrohydrodynamics (Rosensweig et al.,1985).Because of its distinct fluidic and magnetic properties researchers started exploiting it to create wonders.

Ferrofluids are colloidal liquids made of nanoscale ferromagnetic, or ferrimagnetic, particles suspended in a carrier fluid(usually an organic solvent or water). Each tiny particle is thoroughly coated with a surfactant to inhibit clumping. Large ferromagnetic particles can be ripped out of the homogeneous colloidal mixture, forming a separate clump of magnetic dust when exposed to strong magnetic fields. The magnetic attraction of nanoparticles is weak enough that the surfactant's Van der Waals force is sufficient to prevent magnetic clumping or agglomeration. Ferrofluids usually do not retain magnetization in the absence of an externally applied field and thus are often classified as "superparamagnets" rather than ferromagnets (Voit et al., 2011).

The difference between ferrofluids and magnetorheological fluids (MR fluids) is the size of the particles. The particles in a ferrofluid primarily consist of nanoparticles which are suspended by Brownian motion and generally will not settle under normal conditions. MR fluid particles primarily consist of micrometre-scale particles which are too heavy for Brownian motion to keep them suspended, and thus will settle over time because of the inherent density difference between the particle and its carrier fluid. These two fluids have very different applications as a result.

2. SYNTHESIS OF FERROFLUIDS

Ferrofluids are composed of nanoscale particles (diameter usually 10 nanometers or less) of magnetite, hematite or some other compound containing iron, and a liquid. This is small enough for thermal agitation to disperse them evenly within a carrier fluid, and for them to contribute to the overall magnetic response of the fluid. This is similar to the way that the ions in an aqueous paramagnetic salt solution (such as an aqueous solution of copper (II) sulfate or manganese(II) chloride) make the solution paramagnetic. The composition of a typical ferrofluid is about 5% magnetic solids, 10% surfactant and 85% carrier, by volume.

EvrimKurtoglu et al., 2012, synthesized ferrofluid by co-precipitation of aqueous solutions of $FeCl_2$ and $FeCl_3$ in a basic environment. Using fine control of the addition rate of the reactants to the reaction vessel considerably small and uniform particle sizes are achieved easily. To prevent aggregation and to facilitate their motion inside the liquid, nanoparticles of SPIO were coated with lauric acid, which contributes to the long-term stability of the nanofluid. The sizes of the ferromagnetic nanoparticles in the sample SPIO-LA are 20–30 nm. This lab-made sample of Lauric acid-coated super paramagnetic Iron oxide (SPIO-LA) was used as the ferrofluid in their studies.

Patricia Berger et al.,1999, combined 1.0 mL of stock $FeCl_2$ solution and 4.0 Ml of stock $FeCl_3$ solution. Then they placed a magnetic stirring bar in the flask and begin stirring vigorously. Then drop wise addition of 50 mL of 0.7 M aqueous NH_3 solution into the flask was done. They have found that the slow rate of addition is critical, and a pipet or burette is a convenient means of slowing the addition rate. Magnetite, a black precipitate formed immediately. Stirring was done throughout the addition of the ammonia solution. Then stopped stirring and allowed the precipitate to settle (5–10 min),then decanted and disposed of most of the liquid. Stirred the remaining solution and centrifuged the solution for 1 min at 1000 rpm. This was to obtain an adequate amount of solid magnetite for preparing a ferrofluid sample. Decanted the supernatant after centrifugation. The dark, sludge like solid at the bottom of the tube was magnetite. Then they have divided 8 ml of 25% tetramethyl ammonium hydroxide solution among the centrifuge tubes used during the centrifugation and stirred with a thin glass rod until the solid is completely suspended in the liquid. Then they have poured the contents of all of the tubes into a vacuum filtration flask, added a magnetic stirring bar, and stopper the flask. Magnetically stirred the solution under aspirator vacuum for 30 min to remove excess ammonia from the solution. After stirring, slowly poured the liquid into a beaker. The magnetic stirring bar that remained in the filtration flask should be covered with a black sludge, which may or may not exhibit spikes at the ends of the magnet. Then they have gently poured the stirring bar and attached sludge into a plastic weighing boat. Then they have removed the magnetite from both ends of the stirring bar.

Jyotsnendu Giriet al., prepared the substituted ferrites by co-precipitation technique in N_2 atmosphere. The double distilled water was purged with N_2 during 2 h before use for metal ions solutions preparation. They have quickly added one hundred and twenty milliliters of metal ions solution (0.2M) to the ammonium hydroxide solution (350 ml) with vigorous stirring (3000 rpm) and pH of the resultant reaction mixture. During heating, the pH was monitored and kept constant by addition of a base (ammonium hydroxide). The as-prepared slurry was cooled to room temperature and kept for 5 min on a permanent magnet (0.2T surface fields) to accelerate the settling process. The supernatant of the reaction mixture was decanted. The precipitate was repeatedly washed with 5–10% (w/v) NH_4OH (25%) solution to remove any impurity ions. The part of the slurry was washed with acetone and dried at room temperature for further characterization. The remaining part of the material was used for ferrofluid preparation. The wet-washed ferrites nanoparticles of various compositions obtained from above synthesis procedure. They have centrifuged the ferrofluid at 5000 rpm for 15 min to separate out the unstable particles followed by purification process. The average particles size (hydrodynamic diameter) of the lauricacid-coated magnetic particles was 80nm. The excess lauricacid and NH_4+ ions were removed by dialysis of ferrofluid against distilled water using cellulose membrane (12.4 kDa) for 72 h. The pH of resultant ferrofluids was 7.4.These fluids were again centrifuged at 3500 rpm for 15 min. Then, the ferrofluids were filtered using the Whatman 2 (qualitative) and kept for further characterizations.

Luis Martinez et al., 2005 synthesized ferrofluid based on the reaction of iron ions in an aqueous ammonia solution. The resulting magnetite is then mixed with aqueous tetramethyl ammoniumhydroxide $(CH_3)_4NOH$solution, which acted as a surfactant to the nanoparticles by absorption of the OH anion on the surface and the surrounding tetramethyl ammoniumcations as the electrostatic repulsion agent. The overall synthesis process is shown in Fig. 1.adopted from Luis Martinez et al., 2005

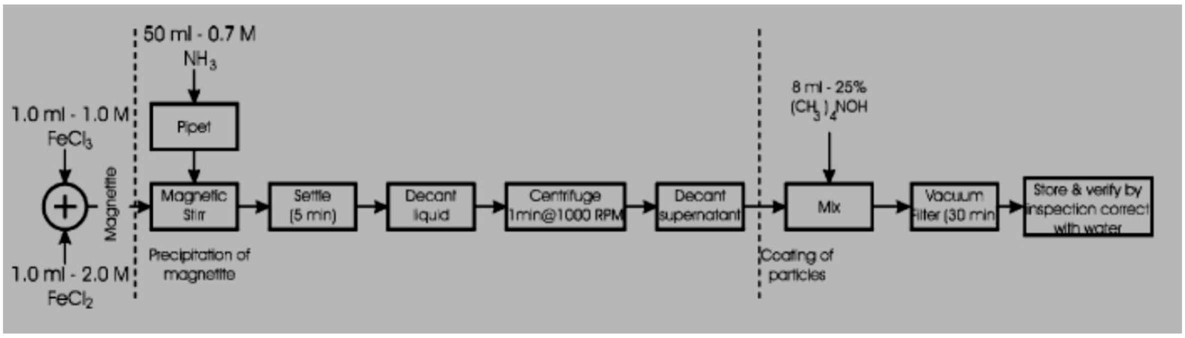

Figure 1. The synthesis process of ferrofluid, adapted from Luis Martinez et al., 2005

S. Masoud Hosseini et al., 2012, prepared Ferrofluids by mixing 20 g of Co_3O_4nanopowder with 50 cc of OA. The OA was added to the nanoparticles as a capping agent and to improve the dispersion of nanoparticles in the prepared ferrofluids. OA has been successfully used previously for Fe_2O_3 nanoparticles to ensure that the nanoparticles remain unagglomerated during testing (Ghasemi et al.2008). The mixture was then milled in a Fritsch Pulverisette model planetary mill for 5 h to ensure that the particles are well capped. A series of stable nanoparticle suspensions in liquid paraffin having different particle concentrations were then made by: (1) adding an appropriate amount of paraffin and OA; (2) mechanically mixed them; and (3) sonicating the suspension in an ultrasonic bath. After characterization the mean nanoparticle size was found to be 21nm.

Ali Abdollahi et al., 2017, had used 1 mL of a $FeCl_2$ solution (2 M solution of $FeCl_2$ in 2 MHCl) which was mixed with 4 mL of $FeCl_3$ (1 M solution of FeCl3 in2 M HCl). Afterwards, 50 mL of 0.7 M ammonia solution has been added with a syringe pump with the rate of 375 ml/h. In the meanwhile of adding ammonia solution, the solution has become darker and magnetic particles have formed. By centrifuging the solution, highly dark sediment remained at the bottom of the test tube. Finally, 8 mL of a 25% tetra-methyl-ammonium hydroxide solution has been added to the sediment to provide the solid-in-fluid suspension after stirring. The nanoparticles has an average diameter of 25 nm for a 0.1%volume concentration nanofluid.

Mohd Imran et al., 2018 worked on the synthesis of ferrofluids using mineral oil as a carrier fluid and oleic acid coated Fe_3O_4 nanoparticles as dispersed phase. Morphology (shape and size) and crystallinity of the synthesized nanoparticle is captured using TEM and XRD. Oleic acid coating on nanoparticle is probed using FTIR for confirming the stability of ferrofluid. Thermal properties of mineral oil based ferrofluid with varying concentration of nanoparticles are evaluated in terms of thermal conductivity. They found that the thermal conductivity of ferrofluid increases upto 2.5% (w/v) nanoparticle loading, where a maximum enhancement of ~51% in thermal conductivity was recorded as compared to the base fluid.

3. APPLICATIONS OF FERROFLUIDS

3.1 Electronics Applications

Ferrofluids are used to form liquid seals around the spinning drive shafts in hard disks. The rotating shaft is surrounded by magnets. A small amount of ferrofluid, placed in the gap between the magnet and the shaft, will be held in place by its attraction to the magnet. The fluid of magnetic particles forms a barrier which prevents debris from entering the interior of the hard drive. According to engineers at Ferrotec, ferrofluid seals on rotating shafts typically withstand 3 to 4 psi; additional seals can be stacked to form assemblies capable of higher pressures.

Jie Yao et al., 2015 presented a novel inertial sensor with a movable nonmagnetic rod immersed in the ferrofluid, which can be used as a low band accelerometer. Movement of the nonmagnetic rod inside a container under the influence of external inertial forces will lead to the change of the ferrofluidic volume distribution. A couple of sensing coils detect the change and a corresponding signal occurs. The nonmagnetic rod with a dumbbell-shaped structure improves the linearity and stability of the sensor. The specially arranged permanent magnets create a non-uniform magnetic field, which generates a powerful restoring force determining the position of the nonmagnetic rod. The restoring force is performed by means of the comparison between experimental measurements and theoretical calculation. Their studies have proved that compared with the conventional ferrofluid inertial sensors, one of the most significant advantages of the proposed device is that it can be applied in the magnetic environment.

Luis Martinez etal., 2005, has synthesized and characterized a novel ferrofluid magneto-optic material. A quantity of 100 ml was manufactured using the charge stabilized method, which proved to be very inexpensive (£ 0.15 per ml) and with very high Verdet constant of 122.43×10^{3} rad T^{-1} m^{-1}. As no linear birefringence was observed, this material is found to be particularly suitable for magneto-optic sensor applications where the presence of electric field is expected, such as detection of mains electrical current.

3.2 Medical and Biomedical applications

Several ferrofluids were marketed for use as contrast agents in magnetic resonance imaging, which depend on the difference in magnetic relaxation times of different tissues to provide contrast (Scherer, C, 2005; Wang, 2011). Several agents were introduced and then withdrawn from the market, including Feridex I.V. (also known as Endorem and ferumoxides, discontinued in 2008; [15] resovist (also known as Cliavist (2001 to 2009, Softways, 2012); Sinerem (also known as Combidex, withdrawn in 2007; [17]Lumirem (also known as Gastromark (1996 to 2012; Clariscan (also known as PEG-fero, Feruglose, and NC100150), development of which was discontinued due to safety concerns.

Ferrofluids have been proposed for magnetic drug targeting. In this process the drugs would be attached to or enclosed within a ferrofluid and could be targeted and selectively released using magnetic fields (Kumar etal., 2011). It has also been proposed for targeted magnetic hyperthermia to convert electromagnetic energy into heat (Kafrounietal., 2016). It has also been proposed in a form of nanosurgery to separate one tissue from another—for example a tumor from the tissue in which it has grown (Scherer et al., 2005).

In medicine, ferrofluids are used as contrast agents for magnetic resonance imaging and can be used for cancer detection. The ferrofluids are in this case composed of iron oxide nanoparticles and called SPION, for "Superparamagnetic Iron Oxide Nanoparticles".

Jyotsnendu Giriaet al.,had utilized the the possibility of biomedical applications of water-based ferrofluids of substituted ferrites. Superparamagnetic particles of substituted ferrites and their fatty acid coated water base ferrofluids have been successfully prepared by co-precipitation technique using NH_4OH/TMAH (Tetra methyl ammonium hydroxide) as base. In vitro cytocompatibility study of different magnetic fluids was done using HeLa (human cervical carcinoma) cell lines. Co2+-substituted ferrite systems (e.g. $CoFe_2O_4$) is more toxic than Mn^{2+}-substituted ferrite systems (e.g. $MnFe_2O_4$, $Fe_{0.6}Mn_{0.4}Fe_2O_4$). The later is as cytocompatible as Fe_3O_4. They have showed that it could be useful in biomedical applications like MRI contrast agent and hyperthermia treatment of cancer.

3.3 Mechanical Engineering Applications

Ferrofluids have friction-reducing capabilities. If applied to the surface of a strong enough magnet, such as one made of neodymium, it can cause the magnet to glide across smooth surfaces with minimal resistance.

Ferrofluids can also be used in semi-active dampers in mechanical and aerospace applications. While passive dampers are generally bulkier and designed for a particular vibration source in mind, active dampers consume more power. Ferrofluid based dampers solve both of these issues and are becoming popular in the helicopter community, which has to deal with large inertial and aerodynamic vibrations. EvrimKurtog˘lu et al., 2012, utilized the potential of magnetically actuated ferrofluids as an alternative micro pumping system. Different families of devices actuating ferrofluids were designed and developed in their study to reveal this potential. A family of these devices actuates discrete plugs, whereas a second family of devices generates continuous flows in tubes of inner diameters ranging from 254 μm to 1.56 mm. The devices were first tested with minitubes to prove the effectiveness of the proposed actuation method. The setups were then adjusted to conduct experiments on microtubes. Promising results were obtained from their experiments. They have achieved the flow rates up to 120 and 0.135 μl/s in minitubes and microtubes with modest maximum magnetic field magnitudes of 300 mT for discontinuous and continuous actuation, respectively. This proposed magnetic actuation method was proven to work as intended and is expected to be a strong alternative to the existing micropumping methods such as electromechanical, electrokinetic, and piezoelectric actuation. The results suggest that ferrofluids with magnetic nanoparticles merit more research efforts in micro pumping.

3.4 Optical Applications

Research is under way to create an adaptive optics shape-shifting magnetic mirror from ferrofluid for Earth-based astronomical telescopes (Philip etal., 2003).Optical filters are used to select different wavelengths of light. The replacement of filters is cumbersome, especially when the wavelength is changed continuously with tunable-type lasers. Optical filters tunable for different wavelengths by varying the magnetic field can be built using ferrofluid emulsion (Hecht et al., 2008).

I. Torres et al., 2014, in their review article describes about the optical applications of ferrofluids. According to their study, common magnetically tunable optical properties studied in ferrofluids are dichroism, birefringence, and the so-called magneto-optic effect. These tunable optical properties of ferrofluids are attributed to the shape anisotropy of the particles or to the formation of chain structures due to the applied magnetic field and magnetic dipole–dipole interactions. Ferrofluid core optical fibers were reported by Zou et al. These have the main advantage of having tunable properties like optical loss and multi-mode operation in an applied magnetic field, as compared to other liquid optical fibers.

3.5 Heat Transfer Applications

An external magnetic field imposed on a ferrofluid with varying susceptibility (e.g., because of a temperature gradient) results in a nonuniform magnetic body force, which leads to a form of heat transfer called thermomagnetic convection. This form of heat transfer can be useful when conventional convection heat transfer is inadequate; e.g., in miniature microscale devices or under reduced gravity conditions.

Ferrofluids are commonly used in loudspeakers to remove heat from the voice coil, and to passively damp the movement of the cone. They reside in what would normally be the air gap around the voice coil, held in place by the speaker's magnet. Since ferrofluids are paramagnetic, they obey Curie's law, thus become less magnetic at higher temperatures. A strong magnet placed near the voice coil (which produces heat) will attract cold ferrofluid more than hot ferrofluid thus forcing the heated ferrofluid away from the electric voice coil and toward a heat sink. This is an efficient cooling method which requires no additional energy input. Ali Abdollahi et al., (2017) in this research, an experimental study was conducted to investigate the pool boiling heat transfer of Fe_3O_4/water nanofluid (ferrofluid) in the atmospheric pressure. They also investigated the influence of the magnetic field on the rate of boiling heat transfer of nanofluid. Deionized (DI) water was used to examine the repeatability, integrity and precision of the experimental apparatus where a well agreement with the existing correlations was observed. The investigation of various volume concentrations of nanofluid revealed that boiling heat transfer in high concentrations decreases with an increase of concentration while it rises with the increase of concentration in low concentrations. The boiling heat transfer coefficient at 0.1% volume concentration nanofluid was evaluated as optimal (increasing up to 43%). In addition, their experimental studies showed that the presence of positive and negative magnetic field gradients decrease and increase the boiling heat transfer, respectively. The findings of their study showed that at higher concentrations of nanofluid, the effect of the magnetic field on nanoparticles is boosted. The results of the experiments indicated that adding nanoparticles would not necessarily increase the boiling heat transfer coefficient. In fact, the surface roughness and the magnetic field gradient on the boiling surface were the main factors that could affect the boiling heat transfer coefficient, significantly.

3.6 Spacecraft propulsion

Ferrofluids can be made to self-assemble nanometer-scale needle-like sharp tips under the influence of a magnetic field. When they reach a critical thinness, the needles begin emitting jets that might be used in the future as a thruster mechanism to propel small satellites such as CubeSats (Raval et al., 2013).

4. CONCLUSION

Ferrofluid's properties make it useful for many different applications. Ferrofluid is used in rotary seals in computer hard drives and other rotating shaft motors. Loudspeakers use ferrofluid to dampen vibrations. In medicine, ferrofluid is used as a contrast agent for magnetic resonance imaging (MRI).In the future, ferrofluids may also be used to carry medications to specific locations in the body. This “ferrofluid” has unique properties because the iron oxide particles are magnetic and thus the fluid can be controlled by a magnetic field. Both magnetic and liquid properties influence the device performance. Ferrofluids synthesized about 30 years previously are still stable. So as per the applications illustrated here, we can conclude that ferrofluid is an exciting area of research in multidisciplinary science and engineering in the present and future world.

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