ABSTRACT

Ferrofluid, a stable suspension of magnetic nanoparticles in the size range of $2 - 10 \, nm$, exhibits a variety of unusual properties. The ability for easy manipulation of these fluids by an external field has led to many innovative applications in mechanical, biomedical, electronic and optical systems. Ferrofluids are now used for many applications such as dynamic mechanical seals, airborne seals for protection of optical devices and sensitive electronic instrumentation in military and surveillance aircraft and stimulant for enhancing chemical reactions. In medical applications, ferrofluid is used as a new cancer treatment agent and iron based nanoparticles are used as delivery vehicles for drugs. Ferrofluid is also effectively used for cell and DNA sorting. In addition, magnetic colloids have been found to be a wonderful model system to study fundamental aspects such as understanding magnetic domain structures, size related studies of crystalline domains; study of phenomena like superparamagnetism and magnetic dipolar interactions.

The requirement of size, morphology and magnetic properties of nanoparticles used in the ferrofluid vary with applications. Similarly the ferrofluids should be sufficiently stable during storage and in use (application). Therefore, the methodologies to control the physical properties of nanoparticles and the stability of ferrofluids are very important. Most commonly used particles for ferrofluid applications are magnetite nanoparticles due to their chemical stability (less sensitive towards oxidation, compared to transition metals), high saturation magnetization value among the ferrites, ease for tagging with bio-molecules and biocompatibility. Therefore, to tailor nanoparticles of desired physical properties, the parameters influencing the composition, size and magnetic properties of magnetite nanoparticles
during co-precipitation have been studied. These experiments are further extended to understand the co-precipitation technique and to develop simple methods to produce ferrite nanoparticles with improved magnetic properties and to understand the polymer-surfactant interactions.

It has been found that the critical equilibrium radius and hence the particle size can be tuned by controlling the dielectric constant of solvent with suitable ratio of ethanol and water. Using this approach, particle size is tuned from 2.3 to 6.5 nm. These experimental results showed that the nucleated particle size is directly proportional to dielectric constant of the solvent, in agreement with nucleation theory.

The effect of alkali addition rate on particle size revealed that the nanoparticles size increases with decreasing alkali addition rate. As alkali addition rate increases, the solution reaches supersaturation state rapidly, leading to the formation of large number of initial nuclei with smaller size at nucleation stage. The average particle size increases from 6.8 to 11 nm when the alkali addition rate is reduced from 80 to 1 ml/sec. During the size increase from 6.8 to 11 nm, the lattice parameter also increased from 0.835 to 0.838 nm, which is attributed to the high surface energy of the nanoparticles and oxidation of surface Fe$^{2+}$ ions.

Temperature dependant precipitation studies showed that the increase in the reaction temperature from 30 to 70 °C, the nucleated particle size increased from 6.8 to 9.8 nm and the saturation magnetization values from 38.7 to 62.9 emu/g.

It has been found that the initial pH (prior to alkali addition) and temperature of the ferrous and ferric salt solution before initiation of the precipitation reaction are critical parameters for controlling the composition and size of the nanoparticles. With increasing initial pH and temperature of iron salt solutions, Fe$^{2+}$ ions deplete due to oxidation (Fe$^{2+}$ + O$_2$ → Fe$^{3+}$) leading to increase in Fe$^{3+}$/(Fe$^{2+}$ + Fe$^{3+}$) ratio towards 1.
Nanoparticles formed are 100% spinel iron oxide, when the initial pH of the salt solution is below 5 and at a final pH (after alkali addition) of below 12.5.

A process to synthesize stable water based and oil based ferrofluids with suitable surfactant coating is developed and an optimization procedure to remove ionic impurities and excess surfactant molecules from the oleic coated particles is discussed. It has been found that the repeated acetone/hexane washings of oleic acid adsorbed magnetite particles leads to desorption of surfactant molecules due to competition between the affinity of the carboxylate group of the oleic acid to the surface of the particle and the organic solvent.

It is found that in magnetite precipitation, a digestion time of 300 sec is sufficient to complete the growth process to attain a thermodynamically equilibrium state with insignificant Oswald ripening due to the domination of a solid state reaction where high electron mobility of Fe$^{2+}$ and Fe$^{3+}$ ions drives a local cubic close-packed ordering.

Ferrite nanoparticles are synthesized by varying the divalent metal ions Mn, Co, Fe and Zn that vary solubility product of respective hydroxides. With increasing divalent metal hydroxide solubility product from $10^{-17}$ to $10^{-13}$, the average size of the nucleated ferrite nanoparticles also increased from 8.9 to 29.1 nm, as demonstrated in nucleation theory. The Mn, Co and Fe ferrites are magnetic in nature with saturation magnetization of 44.6, 47.38, 56.19 emu/g respectively, whereas the Zn ferrite was paramagnetic. These investigations show that the solubility product of the divalent metal hydroxides has significant role on the size and the magnetic properties of the nucleated nanoparticles.

A simple method to produce magnetic nanoparticles with enhanced phase transition temperature from cubic maghemite ($\gamma$-Fe$_2$O$_3$) to rhombohedral hematite
(α-Fe₂O₃) has been developed. The enhancement in phase transition temperature by about 150 °C for 5 nm size nanoparticles is achieved by using NaOH as an alkali. The sodium ions seemed to have got trapped inside the crystal while crystallizing the magnetite nanoparticles with rapid oxidation because atoms or ions need lower activation energy for diffusion in nanocrystalline state. The transition temperature decreased with decreasing particle size due to reduced activation energy of the system.

On thermal annealing at 1000 °C under vacuum, the cations redistribution was observed in ZnFe₂O₄ nanocrystals leading to the lattice parameter decrease from 8.441 to 8.399 Å and increase at saturation magnetization value to 60 emu/g. The observed saturation magnetization value for ZnFe₂O₄ is the highest value reported in literature.

Force measurements between emulsion droplets in the presence of a neutral polymer-poly vinyl alcohol and an ionic surfactant-sodium dodecyl sulphate reveal that the interaction between polymer, surfactant and colloidal drop can lead to three distinct scenarios, depending on the sequence of adsorption of polymer and surfactant onto the colloidal interface. Among these three scenarios, surfactant addition to polymer pre-adsorbed emulsion system provides long term stability for emulsion.