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SYNTHESIS OF MAGNETIC NANOPARTICLES USING REVERSE MICELLES

A Dissertation

Submitted to the Graduate Faculty of the
University of New Orleans
In partial fulfillment of the
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in
The Department of Chemistry

By

Everett E. Carpenter

B.S., Appalachian State University, 1994

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DOCTORAL DISSERTATION REPORT

Candidate: Everett E. Carpenter

Major Field: Chemistry

Title of Dissertation: Synthesis of Magnetic Nanoparticles Using Reverse Micelles

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"For me chemistry represented an indefinite cloud of future potentialities which enveloped my life to come in black volutes torn by fiery flashes, like those which had hidden Mount Sinai. Like Moses, from that cloud I expected my law, the principle of order in me, around me, and in the world. . . . I would watch the buds swell in spring, the mica glint in the granite, my own hands, and I would say to myself: "I will understand this, too, I will understand everything."" Primo Levi (1919–87), Italian chemist, author. *The Periodic Table*, "Hydrogen"

I would like to thank my family and friends for their support and understanding while I pursue my chemistry.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

Nanoparticles are single crystallites or composite materials in which the dimensions are within 1 to 100 nm in scale. Synthesizing nanoparticles with very narrow size distribution and high uniformity is one of the prime goals of this research. To achieve the high uniformity aqueous reactions are carried out using the confined aqueous core of a reverse micelle can be used as a "nano-reactor", thus allowing us to carry on aqueous reactions, such as precipitation reactions, within a confined space and gaining the advantage of size restriction.

We present the magnetic properties of eight different nanoparticles synthesized within reverse micelles. The particles are separated into four chapters depending on their magnetic properties and structure. In chapter one we present the synthesis and magnetic properties of cobalt platinum alloys. These alloys are superparamagnetic and display higher coercivities than cobalt particles of the same size. Alloying displays one method of improving the coercivity of metal nanoparticles.

The synthesis of the antiferromagnetic $KMnF_3$ is presented in chapter two. The synthesis of $KMnF_3$ nanoparticles using reverse micelles is presented for the first time. The particles display a highly uniform cubic structure. The particles display an antiferromagnetic ordering temperature of 88 K and a blocking temperature which varies with particle size between 36 and 10 K.

Aqueous reactions allow for a greater variation of reaction conditions. In chapter three the manganese ferrite nanoparticles synthesized in reverse micelles is presented for the first time. 5 nm $MnFe_2O_4$ are superparamagnetic with a blocking temperature of 33 K. For comparison two other common ferrites, Fe_3O_4 and $CoFe_2O_4$, were also

synthesized. Reaction conditions demonstrated an effect on the overall cation distribution between the A and B sublattice of the spinel. This redistribution did not have a pronounced affect on magnetic properties.

Lastly, a sequential synthesis is presented where iron and gold are grown in core-shell and "nano-onion" like structures. These particles have the favorable magnetic properties of iron while remaining protected from oxidation by a gold shell. The effect of the gold shell on the magnetic properties of coercivity and blocking temperature is discussed. Although the thickness of the gold shell is varied between 2 and 3 nm, there is not a change in the coercivity or blocking temperature within experimental error. In addition, the electronic properties of the "nano-onions" were studied. Gold-Iron-Gold nano-onions display a –1.5 % magnetoresistance. The particles undergo a transition from itinerate to localized electrons resulting in a 400 % increase in resistance as the particles are cooled to 10 K.

CHAPTER 1, INTRODUCTION

1.1 Preface

Nanoparticles are materials that have grain sizes less than 100 nanometers. Interest in nanoparticles has grown over the past two decades due to changes in the physical, electronic, magnetic, and optical properties resulting from the small grain size. As the size of the particles is reduced, much of the bulk-grain behavior changes to resemble atomic size regimes. It is this change in bulk-properties which has fueled an explosive growth in nanophase research. Magnetic materials that have nanoscale dimensions are of particular interest.

Magnetic nanoparticles have a wide range of applications. One of the most aggressively pursued areas is in high-density magnetic memory. Areal density in longitudinal magnetic recording has surpassed the 1 Gbit/in^2 level and continues to grow at an impressive rate each year. Current media are composed of CoPtCr alloys due to the low noise and high coercivity. In order to push the areal density even higher, it is important to engineer magnetic materials which have a higher intrinsic coercivity while maintaining low intergrain exchange coupling.[1]

Soft magnetic ferrites, such as Fe_3O_4 and Fe_2O_3, offer many advantages in radio frequency applications where the complex permeability can be modified by external fields or by changing the composition. The flexibility offered during the synthesis of ferrites allows for versatility in applications as rf filters. The radio noise characteristics of the ferrite filters made from nanocrystalline alloy materials are superior due to their increased attenuation range.[2]

Nanophase magnetic materials have many applications outside those of the telecommunications and computer industries. Magnetic materials with a grain size less than 100 nm can be stabilized as ferrofluids. Ferrofluids are magnetic colloid solutions that are used everywhere from high-end consumer speakers to gas valve sealing and lubrication. The ferrofluids are held in place by a large magnetic field, thereby gaining the advantages of both contact and hydrodynamic seals.[3]

It was this vast range of applications for magnetic nanoparticles that prompted the lofty goal of achieving improved magnetic properties using nanoparticles. With this in mind, attention was turned toward determining which synthesis method would help reach this goal. Hopefully along the way, a greater understanding of the magnetic properties of nanoparticles could be attained.

1.2 Synthesis Methods

1.2.1 Introduction

Many of the advantages of nanoparticles are enhanced by narrow size distributions and uniform morphology. For example, in the case of magnetic memory, the noise level between grain boundaries is increased with high levels of dispersion in sizes. There are many different synthesis methods for magnetic nanoparticles. In general, the synthesis techniques can be broken down into two categories, physical and chemical methods. In physical methods, a bulk precursor is physically broken down into smaller grain sizes. In chemical methods, the particles are synthesized via chemical reactions in nanophase dimensions.[4]

There are several different physical methods for preparing nanoparticles, such as attrition[5], sputtering[6], and ablation.[7] Mechanical attrition, such as ball milling, is a non-equilibrium process that can produce a wide range of alloys and composites which cannot be prepared in conventional methods. Sputtering and ablation both rely on the evaporation of a target and subsequent condensation on the substrate. In sputtering the evaporation is achieved using an electric arc while ablation relies on a high energy laser to evaporate the target. Both sputtering and ablation can be adapted to generate a variety of metals, oxides, or salts. Physical methods have a high degree of versatility; however they typically do not generate highly uniform nanoparticles.

A wide variety of chemical methods have been used to synthesize nanoparticles such as precipitation[8], reduction[9], pyrolysis[10], and hydrothermal reactions.[11] In precipitation and reduction methods, the nanoparticles are synthesized by rapid chemical reaction and quenched to limit or prevent crystallization. In pyrolysis, volatile organometallics, like $Fe(CO)_5$, are used and the ligands removed by thermal decomposition to yield the nanoparticles. In hydrothermal synthesis, aqueous reactions are carried out at elevated temperatures and pressures. Since the early 1980's, a growing area of chemical synthesis involved surfactants.[12]

1.2.2 Surfactants

Surfactants get their name from the acronym "surface acting agent". They are used to help affect the surface tension along interfaces. Surfactant molecules contain a long chain hydrocarbon plus a hydrophilic end. Typically the hydrophilic end group comes in the form of an ionic group, such as a sulfate or quaternary amine, forming either anionic or cationic surfactants, respectively. Nonionic surfactants having either ethers or

alcohol functional groups are also common. This combination of polar and non-polar groups allows the surfactant to help solubilize water within an organic medium.[13]

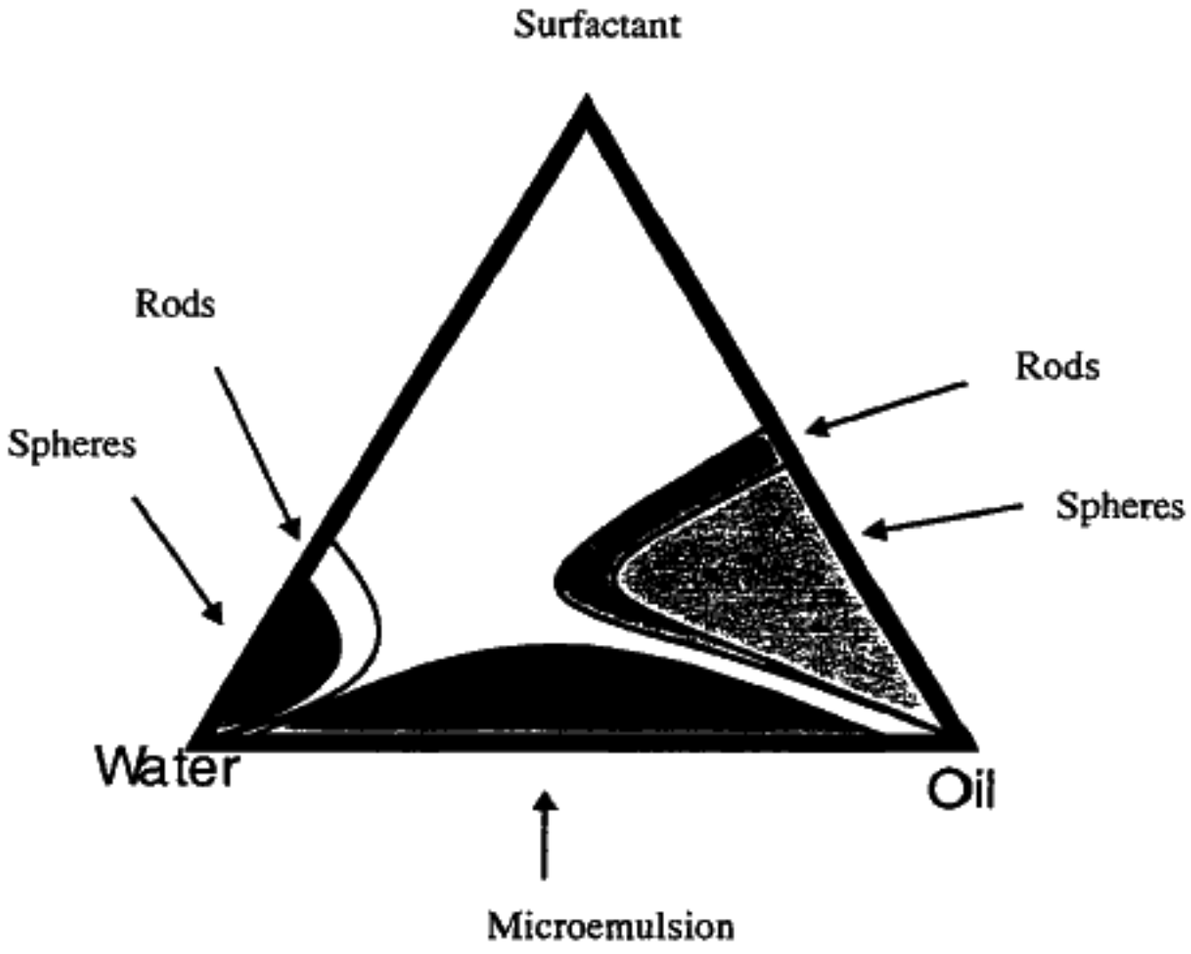
One interesting phenomenon in a water-oil-surfactant system is the presence of self-assembled arrays of surfactants called micelles. In 1963, Winsor noted that certain mixtures of oil, water, and surfactant yielded a clear, seemingly one-phase system.[14] This system, called a micelle or microemulsion solution, contained small droplets of one liquid dispersed within the other with a self-assembled layer of surfactant molecules along the interface between the phases. The self-assembly is driven by thermodynamic factors to minimize surface tensions.[15] Micelle solutions were originally characterized with a bulk aqueous phase where the hydrophobic carbon chains were turned inward to help stabilize the oil phase. Later, reverse micelles were also characterized where the conditions were reversed.[13] A bulk oil phase was used with the hydrophilic head groups turned inward to help stabilize the water phase. A representative three component phase diagram is presented in Figure 1.1.

Micelles exist in very specific conditions dictated by the molar ratio of oil, water, and surfactant. However, the formation of micelle solutions is driven by the differences in the polarity of the two groups; any factor which affects the polarity such as temperature, co-surfactants, or salt concentration also affect the stability of the micelle solution. If the ratio of water to surfactant concentration changes greatly the micelle solution becomes unstable forming a traditional emulsion solution.

1.2.3 Micelles

When surfactants are dissolved in organic solvents they form spherical aggregates called reverse micelles. Micelles can be formed both in the presence and absence of

Figure 1.1. Schematic phase diagram of a surfactant-oil-water system. The areas nearest the lower corners are regions which are characterized by spherical micelles, moving out from there are regions of rod-like microemulsions. The lower region between water and oil is a characteristic macroemulsion region


Surfactant
Rods
Spheres
Rods
Spheres
Water
Oil
Microemulsion

water, however in the absence of water they are very small. When water is added, it is readily solubilized into the polar area of the micelle forming a water pool. This water pool is characterized by ω, the molar water to surfactant ratio ($\omega = [H_2O]/[S]$). Typically aggregates containing a small amount of water (below ω=15) are usually called reverse micelles while microemulsions correspond to droplets containing large amounts of water molecules.[16] This distinction between micelle and microemulsion is often times blurred and the two terms are used interchangeably.[15]

The spherical nature of the surfactant aggregates in reverse micelles is a response to a thermodynamically driven process. It basically represents a need for the surfactants to reach an energetically favorable packing configuration at the interface depending on the molecular geometry of the surfactant.[17] The surfactant molecules can be represented as a truncated cone whose dimensions are determined by the hydrophilic and hydrophobic parts of the surfactant. This geometry is presented in Figure 1.2.

Assuming water-in-oil droplets are spherical, the radius of the sphere is expressed as:

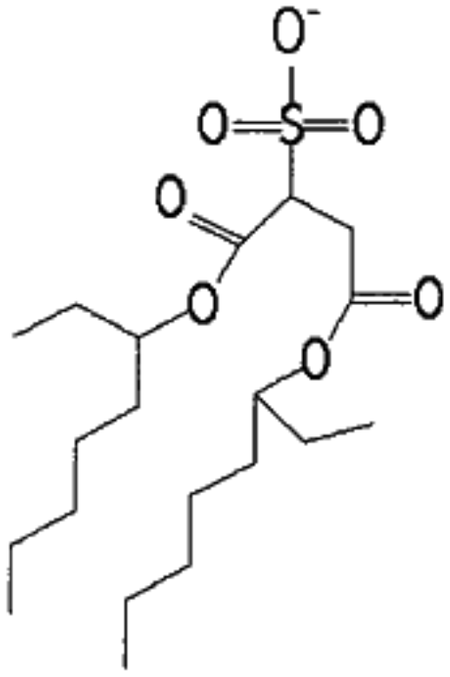
$$R=3V/\Sigma$$

where, R is the radius, V is the volume, and Σ is the surface area. Assuming that the water molecules govern the volume and the surfactant molecules determine the surface area then the water pool radius can be expressed as:

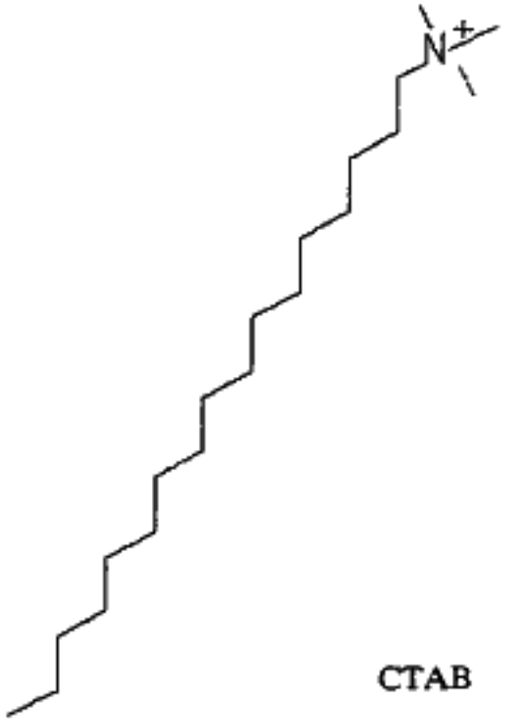
$$R_w=3V_{aq}[H_2O]/\sigma[S]$$

where R_W is the radius of the water pool, V_{aq} is the volume of water molecules and σ is the area per polar head group of surfactant.

Figure 1.2. Chemical Representation of two surfactants used in the following chapters. AOT (dioctylsulfosuccinate sodium salt) and CTAB (cetyltrimethylammonium bromide).



AOT



CTAB