

# **EFFECT OF 1-HEXANOL CO-SURFACTANT ON THE NiFe NANOPARTICLES DENSITY IN REVERSE MICROEMULSION SYSTEMS**

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## **ABSTRACT**

In this work, NiFe nanoparticles with molar ratio (1:1) have been synthesized through inverse microemulsion method using water, sodium dodecylbenzenesulfonate as surfactant, toluene as continuous phase, sodium borohydride as reductant agent and citric acid as stabilizing agent, studying the effect on the density of NiFe nanoparticles by the addition of co-surfactant 1-hexanol, thus NiFe (1:1)-A (without 1-hexanol) and NiFe (1:1)-B (with 1-hexanol) were analyzed. The NiFe microemulsion systems was characterized by means atomic absorption (AA), dynamic light scattering (DLS), scanning transmission electron microscopy (STEM) and energy-dispersive x-ray spectroscopy (EDS). The effect of the co-surfactant showed greater stability in the microemulsion, obtaining a higher density of NiFe nanoparticles in comparison with the microemulsion without 1-hexanol. In both microemulsions, nanoparticles with spherical morphology with diameters less than 20 nm were obtained.

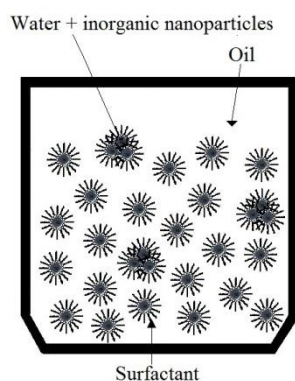
**Keywords:** Inverse microemulsion, NiFe nanoparticles, co-surfactant, 1-hexanol

## **1. Introduction**

Microemulsions (ME) consist of at least three components: polar dispersed liquid phase (water), continuous non-polar liquid phase (hydrocarbon) and surfactant. Some characteristics of these multicomponents are isotropic, optically transparent, they are thermodynamically stable systems and they form drop sizes in the range (1-100) nm. In order to obtain a reverse microemulsion with inorganic compounds as precursor salts within the dispersed phase, several surfactants are used: Sodium dodecyl sulfate (SDS), cetyl trimethyl

ammonium bromide (CTAB), dioctyl sodium sulfosuccinate (AOT), and non-polar phases are generally added (cyclohexane, dodecane, decane, hexane, and heptane) and in some cases co-surfactants of short chain aliphatic alcohols (n-hexanol, n-pentanol and n-butanol) [1-7]. W/O water-in-oil microemulsions are characterized by their droplets being conceived as small nano-reactors, occupying the nucleus where it is possible to find the inorganic nanoparticles and the surfactant forms the shell of the micelle (Fig. 1). The surfactants used in reverse microemulsions are characterized by being amphiphilic molecules, where the polar chain or with

ionic groups interacts strongly with water, while the hydrocarbon chain interacts weakly with water [8-9].



**Fig. 1** Components of a reverse microemulsion (W/O).

The use of co-surfactants in a microemulsion system provides a greater yield to the surfactant and micellar stability. Several works have reported obtaining nanoparticles by the inverse microemulsion method. Kanda and Saranporn [10], prepared nanoparticles of  $\text{Fe}_2\text{O}_3$  with particle size less than 100 nm by the W/O method, using n-heptane as oil phase, water and AOT as surfactant and iron (III) chloride as metal precursor salt; The nanoparticles were produced in situ the water core. Liu and Zhang [11] synthesized nanoparticles of  $\text{MnFe}_2\text{O}_4$  (4-14 nm), by the reverse micelle method using water in toluene and sodium dodecylbenzenesulfonate (NaDBS) as surfactant. Han and coworkers [12] synthesized NiO nanoparticles for the preparation of a microemulsion with cyclo-hexane, triton X-100 and n-hexanol were used as oil phase, surfactant and co-surfactant respectively; concluding that the size of the nanoparticles is strongly affected by the value of the water / surfactant ratio (R) and the calcination temperature. López Quintela and coworkers [13] reported the effect of the co-surfactant on the final particle size, concluding that the addition of a co-surfactant promotes a greater fluidity of the interfacial barrier, while increasing the speed of intermicellar exchange, but also promoting a greater curvature of the drops and therefore smaller particles. In this work we evaluated the

inverse microemulsion method for obtaining transition metal nanoparticles Ni and Fe, which was prepared in two ways with and without co-surfactant: water/toluene/NaDBS/citric acid and water/ toluene/ NaDBS/ 1-hexanol/ citric acid, where it was observed that the use of the co-surfactant 1-hexanol provided greater stability and density of nanoparticles in the microemulsion, in addition to obtaining slightly nanoparticles small and agglomerated.

## 2. Experimental

### 2.1 Chemicals

Nickel (II) nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 99.999%), iron (III) nitrate nonahydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 99.99%), sodium borohydride ( $\text{NaBH}_4$ , 99%), sodium dodecylbenzenesulfonate ( $\text{C}_{18}\text{H}_{29}\text{NaO}_3\text{S}$ , technical grade), 1-hexanol ( $\text{C}_6\text{H}_{14}\text{O}$ , >99%) were purchased by Sigma-Aldrich. Citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ , 99.5%) and toluene ( $\text{C}_6\text{H}_5\text{CH}_3$ , 99.5%) were supplied by Fermont. Ultrapure water ( $15 \text{ M}\Omega\text{cm}^{-1}$ ) was produced by Purelab Option Station.

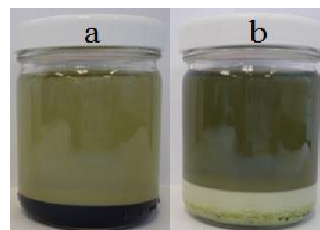
### 2.2 Synthesis of NiFe(1:1)-A and NiFe(1:1)-B

The synthesis of the NiFe nanoparticles was carried out by means of the microemulsion method in reverse micelle starting from the preparation of solution A with nickel (II) nitrate hexahydrate and iron (III) nitrate nonahydrate adding citric acid as stabilizer and sodium borohydride as reducing agent. Solution A was then incorporated into solution B which is composed of sodium dodecylbenzenesulfonate (NaDBS) as an anionic surfactant, with and without 1-hexanol as co-surfactant and toluene as organic solvent. Initially a solution 4M  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and a solution 4M  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were prepared.

The synthesis of the reverse microemulsion without co-surfactant 1-hexanol NiFe (1:1)-A and the inverse microemulsion with co-surfactant 1-hexanol of NiFe (1:1)-B is described below:

For NiFe(1:1)-A, the solution A was prepared by adding to a 50 mL flask, 7.14 mL of ultrapure water, followed by the amount of 2.18 mL of the solution 4M of nickel (II) nitrate hexahydrate applying mechanical stirring for 10 min, then 2.18 mL of the solution 4M of iron (III) nitrate nonahydrate was added followed by 10 min of agitation. Subsequently, 1.65 g of citric acid were added and stirring was kept for 45 min, then 3.5 mL of solution 5M of NaBH<sub>4</sub> was added drop wise with mechanical stirring for 30 min. After reduction with NaBH<sub>4</sub>, solution B was prepared, which consisted of the mixture of 70 g of toluene and 15 g of NaDBS, stirring for 30 min. Solution A is then added dropwise to solution B. The resulting mixture was kept under stirring for a further 120 min, during the last 90 min of stirring the mixture was maintained at a temperature of 50 °C. The mixture was allowed to stand for 48 hours, forming a system with two phases as shown in Fig. 2 (a), then the oil phase (upper part) was separated with the content of the nanoparticles.

For the microemulsion NiFe (1:1)-B, solution A was prepared as NiFe (1:1)-A. After reduction with NaBH<sub>4</sub>, solution B was prepared, which consisted of the mixture of 70 g of toluene, 10 g of NaDBS and 5 g of 1-hexanol stirring for 30 min. Solution A is then added dropwise to solution B. The resulting mixture was kept under stirring for a further 120 min, during the last 90 min of stirring the mixture was maintained at a temperature of 50 °C. The mixture was left to stand for 48 hours, forming a system with two phases as shown in Fig. 2 (b), finally the oil phase (upper part-green color) was separated with the content of the nanoparticles. Table 1 shows the molar ratio of NiFe and the total amounts of the components of both microemulsions.



**Fig. 2** (a) NiFe(1:1)-A (without 1-hexanol) and (b) NiFe(1:1)-A (with 1-hexanol).

**Table 1** NiFe molar ratio and percentages by weight of surfactant, co-surfactant, continuous phase and water contained in NiFe (1:1)-A and NiFe (1:1)-B.

Sample	Molar ratio (NiFe)	NaDBS (wt%)	C <sub>7</sub> H <sub>8</sub> (wt%)	C <sub>6</sub> H <sub>14</sub> O (wt%)	H <sub>2</sub> O (wt%)
NiFe(1:1)-A	1:1	15	70	0	15
NiFe(1:1)-B	1:1	10	70	5	15

## 2.2 Characterization of Materials

In order to determine the concentration of the metals, an atomic absorption spectrophotometer Analyst 300 - Perkin Elmer was used; the sample to be analyzed was obtained directly from the oil phase. The average size distribution of the nanoparticles was determined by dynamic light scattering (DLS) using the Zeta Sizer nano S equipment from Malvern Instruments; a sample of 1.5 mL of microemulsion was used directly in the cell of the equipment. Scanning in light-field transmission electron microscopy (STEM) images and the X-ray energy dispersion spectroscopy (EDS) spectra were obtained using the JEOL JSM-7600F scanning electron microscope and an EDS detector from Oxford Instruments operating at 30 keV in TED mode. For the preparation of the samples, 20 mL of sample of the oil phase recovered from the microemulsion containing nanoparticles (upper part) was mixed with 20 mL of methanol to aid in the precipitation of the material, the mixture was stirred, then centrifuged at 6000 rpm, the precipitate was washed three times with toluene,

removing solvent and surfactant, then washing with chloroform and methanol (1:1) and finally the sample was deposited on a copper grid, followed by a dried at room temperature. The particle size distribution (PSD) was carried out by counting 200 particles contained in the microemulsions.

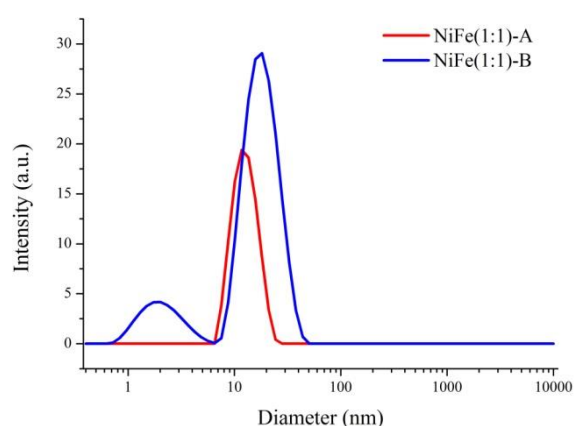
### 3. Results and Discussion

#### 3.1. Atomic absorption results

According to the atomic absorption technique, NiFe (1:1)-A has a (1:0.43) molar ratio while the microemulsion sample where the co-surfactant 1-hexanol was used shows a molar ratio of (1:0.95). The influence of the co-surfactant is remarkable in the stability of the micelles suspended in the continuous phase as can be seen in Fig. 2 (b), where NiFe (1:1)-B presents a dark green color on top of the characteristic microemulsion of the metals suspended in the micelles, in the lower part a slurry type with NaDBS surfactant residue can be observed. NiFe (1:1)-A without the presence of co-surfactant showed less metal retention in the micelles, precipitating more than 50% of the metals. In this case it is possible that the Van der Waals forces present in the amphiphilic chains of the surfactant and continuous phase, are insufficient and overcome by the force of gravity exerted by the particles; moreover, it is likely that the metal particles within the micelles have the size of the drop formed as the growth limit, where the repulsion forces between the particles may be weak, which caused the flocculation of the large particles or agglomerated, only the smallest nanoparticles remain in the core of the micelles suspended in the continuous phase as can be seen in Fig. 2 (a).

#### 3.2. Analysis by dynamic light scattering

Fig. 3 shows the DLS spectra of our prepared materials that determine the metal average particles size (average diameter in nm) in dispersion. For the NiFe (1:1)-A sample a unimodal distribution of particle size can be observed, which diameters oscillate in the range (6-26) nm and centered at 11.6 nm, while that the NiFe (1:1)-B sample shows a bimodal particle size distribution in where most of the particles have average diameters around 17.5 nm and a smaller population is centered at 1.8 nm.



**Fig. 3** Distribution of average particle diameter in NiFe (1:1)-A and NiFe (1:1)-B

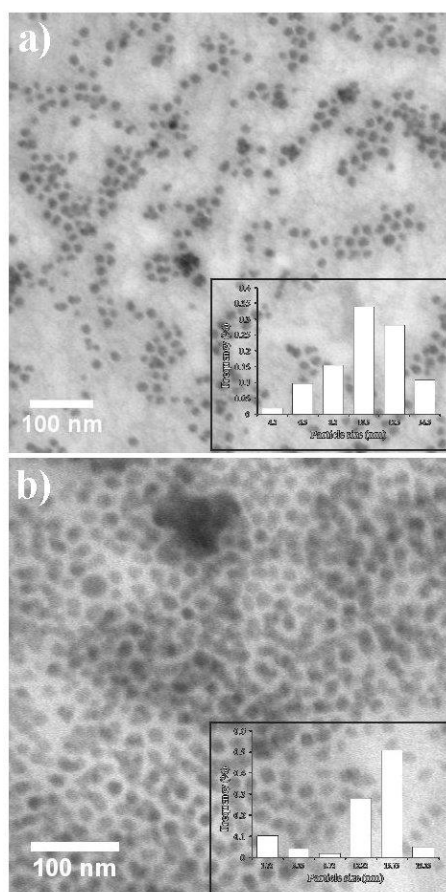
In the DLS spectra a noticeable difference can also be observed between the intensities of the peaks of both materials examined, due to a marked difference in the densities of the particles suspended in the microemulsion; for the NiFe(1:1)-A the influence of surfactant NaDBS was important to achieve a reduced particle size but a poor dispersion of nanoparticles in microemulsion, while for NiFe(1:1)-B the presence of 1-hexanol as co-surfactant shows greater retention of the nano-particles in the micelles but a larger particle size. The difference of the sizes of nanoparticles between both



samples is due to the water / surfactant ratio (R) since the surfactant acts as a stabilizer, spherical impeding agent by inhibiting the agglomeration of the nanoparticles formed in the micelles while a decrease in the same and the addition of a co-surfactant produces small agglomerates and larger nanoparticles [14].

### 3.2. STEM and EDS analysis

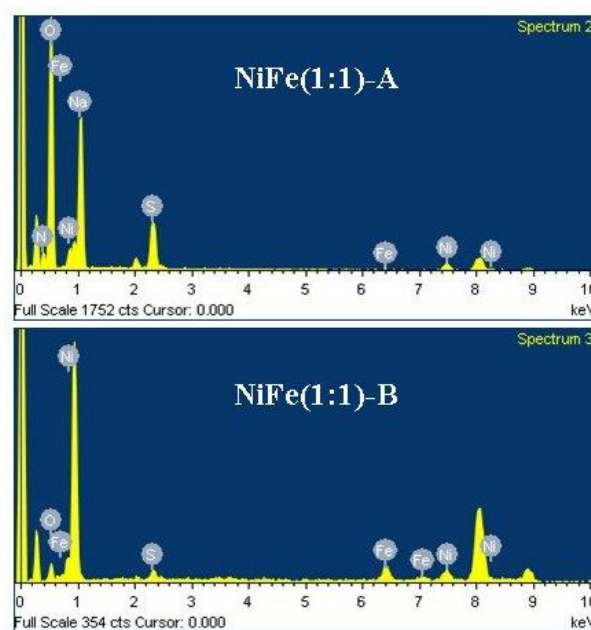
The STEM images at 30 keV and 100,000 X of magnification and PSD's of both micro-emulsions in Fig.4 are illustrated.



**Fig. 4** STEM images and PSD's (inset) of a) NiFe(1:1)-A and b) NiFe(1:1)-B

For NiFe(1:1)-A a poor dispersion of metals nanoparticles which average diameter oscillate in

the range (4-15) nm, while for NiFe(1:1)-B we can be observed a greater density of NiFe nanoparticles which diameter oscillate in the range (2-20) nm. A thorough statistical analysis of the PSD's for both microemulsions reveals that the particle size distribution histogram of NiFe (1:1)-A was significantly drawn from a normally distributed population passing the normality tests Shapiro-Wilk and Kolmogorov-Smirnov for a population distribution with mean of 10.7 nm, while that NiFe (1:1)-B with mean of 12.9 nm, they are not pass these normality test, producing a bimodal particle size distribution according with DLS results. The Fig. 5 shows the EDS spectra of both ME's.



**Fig. 5** EDS spectra of ME's at 20 keV

The EDS spectrum of NiFe(1:1)-A reveals the presence of Ni and Fe furthermore O, Na and S due to surfactant NaDBS; the same elements with exception the Na, appear for NiFe(1:1)-B with different amount. A notable increasing of Fe is observed due to a high NiFe nanoparticles density. Zn and Cu of substrate were omitted.

The quantitative analysis shows that NiFe(1:1)-A obtained a molar ratio of (0.91:0.56), while for NiFe(1:1)-B, (0.95:0.89) in according with AA results.

#### 4. Conclusion

NiFe(1:1)-A and NiFe(1:1)-B samples were successfully synthesized by the reverse microemulsion method. In the NiFe(1:1)-B sample, the decrease in the surfactant and the addition of 1-hexanol as a co-surfactant produced a greater retention of the metal nanoparticles in the aqueous medium, increasing of the NiFe nanoparticles density within microemulsion.

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