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Preparation and properties of water-based magnetic fluids

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Abstract

Stable suspensions of superparamagnetic iron oxide nanoparticles in water (water-based ferrofluids) were prepared using citric acid (CA) as a surfactant. The influences of different factors on the amount of nanoparticles in a stable suspension were systematically studied. These factors, including the temperature, the pH value and the concentration of CA applied during the adsorption of the CA onto the nanoparticles and during their suspension in water, were evaluated. The highest content of nanoparticles in a stable suspension was obtained when the CA was absorbed at pH values of around 5.2, where two carboxyl groups are dissociated, and when the nanoparticles were suspended at a pH of around 10, where all three carboxyl groups of the CA are in a dissociated state.

1. Introduction

Magnetic fluids or ferrofluids are stable suspensions of superparamagnetic nanoparticles in various carrier liquids. For technical applications these magnetic nanoparticles are usually coated with oleic acid and suspended in non-polar carrier liquids. The monolayer of oleic acid molecules at the nanoparticle surfaces sterically prevents their agglomeration, even with relatively large contents of nanoparticles, thus providing long-term stability of concentrated ferrofluids with good magnetic properties [1]. Recently, water-based ferrofluids have attracted a lot of interest because of their potential in medical applications [2–4]. In such applications the magnetic iron oxide nanoparticles are normally used in the form of stable water suspensions, and the nanoparticles in these suspensions must remain suspended in moderate magnetic fields. A different strategy should be used to ensure suspension stability in the case of a polar carrier liquid, such as water, with that used for non-polar media. Generally, it is more difficult to ensure the stability of water-based suspensions than suspensions in non-polar media, and so much lower contents of magnetic nanoparticles can be suspended. Usually, electrostatic repulsive forces between the nanoparticles related to a high electric surface charge are used to provide the long-term stability. The surface charge can be engineered

simply by changing the pH value of the suspension [5, 6] and/or by the absorption of various polar molecules on the nanoparticles' surfaces. Additionally, surfactant molecules can simultaneously provide steric repulsive forces. Typically, the surfactant molecules are water soluble and have more than one functional group; with at least one functional group they attach themselves to the nanoparticle surface, while the other functional groups ensure the hydrophilic nature of the nanoparticles. Different polar molecules have been used in water-based ferrofluids, including dextran and its derivatives [7], peptides [8] and also citric acid (CA) [9]. CA has three carboxyl groups and one hydroxyl group. On the basis of a FTIR analysis, Sahoo *et al* [9] suggested that citric acid chemisorbs to the iron oxide nanoparticles by forming a carboxylate complex with the surface Fe ions. In the present work, the influences of different experimental conditions on the adsorption of CA on iron oxide nanoparticles and consequently on the content of the nanoparticles in the finally prepared water-based ferrofluid were systematically studied.

2. Experimental details

Maghemite nanoparticles were precipitated from an aqueous solution of FeSO_4 (0.027 mol l^{-1}) and $\text{Fe}_2(\text{SO}_4)_3$ ($0.0115 \text{ mol l}^{-1}$) with a concentrated ammonia solution (25%)

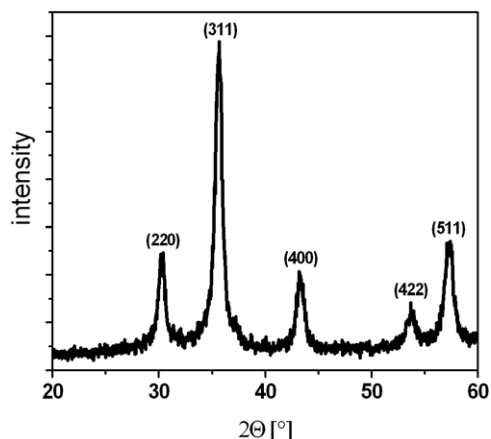


Figure 1. XRD pattern of the synthesized nanoparticles.

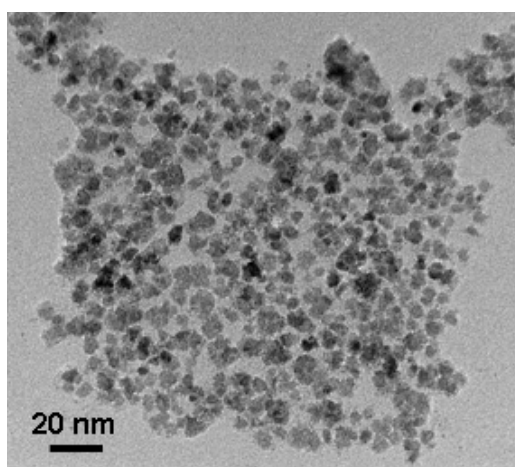


Figure 2. TEM image of the synthesized nanoparticles.

in a two-step process. In the first step, the pH value of the solution was raised to $\text{pH} = 3$ and maintained at a constant value for 30 min to precipitate the iron hydroxides. In the second step, the pH value was further increased to $\text{pH} = 11.6$. In this step the iron (II) hydroxide was oxidized by oxygen from the air, forming a spinel product. After an ageing time of 30 min the iron oxide particles were magnetically separated and washed several times using a diluted ammonia solution with a high pH value of 10.5 to provide a high, negative surface charge on the nanoparticles (see the changing of the zeta potential with pH, presented in figure 3), thus preventing any strong agglomeration during their washing. The dried, as-synthesized nanoparticles were characterized with x-ray powder diffractometry (XRD) (Bruker AXS, D4 ENDEAVOR) and transmission electron microscopy (TEM) (JEOL 2010F). The size of the nanoparticles was determined from TEM images and with Scherrer's method, based on the broadening of the peaks in the XRD pattern using *Diffra^{plus} TopasTM* software.

The crucial step in the preparation of a water-based ferrofluid is the adsorption of the CA surfactant on the nanoparticles. Approximately 2 g of the washed nanoparticles were mixed with 65 ml of the aqueous solution of CA. Then the pH value of the mixture during the adsorption step was adjusted with concentrated ammonia and rigorously stirred

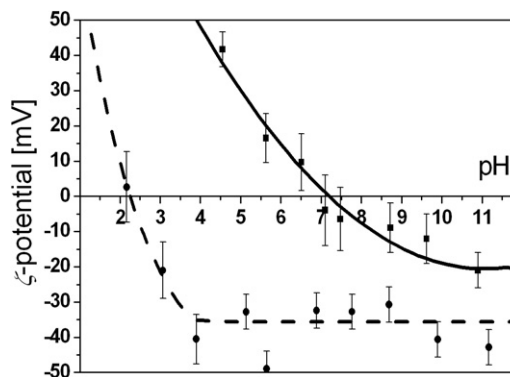


Figure 3. Zeta potential curves of maghemite particles (—) and maghemite particles coated with CA (- - -).

at a constant temperature. In order to study the influence of the applied experimental conditions on the efficiency of the adsorption process, the concentration of CA ($\gamma(\text{CA})$), the pH value (pH_{ads}), and the temperature (T_{ads}) used during the adsorption step were varied from $\gamma(\text{CA}) = 0.05 \text{ g ml}^{-1}$ to $\gamma(\text{CA}) 0.04 \text{ g ml}^{-1}$, from $\text{pH}_{\text{ads}} = 2$ to 11 and from $T_{\text{ads}} = 20^\circ\text{C}$ to 80°C , respectively. After 90 min, allowed for the adsorption of the citric acid, the mixture was cooled down to room temperature. The nanoparticles were then suspended simply by adjusting the pH value of the mixture. The pH during the suspending step (pH_{susp}) was adjusted to different values, ranging from $\text{pH}_{\text{susp}} = 7$ to 10.7, with concentrated ammonia. The prepared suspension was centrifuged for 5 min at 5000 r min^{-1} to remove any agglomerated particles. The content of magnetic nanoparticles in the stable suspension (w) after centrifugation, defining the magnetic strength of the ferrofluid, was used as a criterion for the efficiency of the preparation procedure.

The compositions of the ferrofluids were determined with thermogravimetric measurements. The specific magnetization of the materials at room temperature was measured using a vibrating-sample magnetometer (Lake Shore 7307), and the temperature dependence of magnetization was determined under zero-field cooling (ZFC) and field cooling (FC) ($H = 100 \text{ Oe}$) conditions in the temperature range between 2 and 350 K using a SQUID (Quantum Design SQUID). The zeta potential was determined with electrokinetic measurements of the nanoparticles' mobility using a zeta-meter (Brookhaven Instruments Corp., ZetaPALS).

3. Results and discussion

The XRD pattern of the as-synthesized nanoparticles (figure 1) showed broad peaks that can be ascribed to the spinel structure. Since a chemical analysis showed that less than 3% of all the iron contained in the nanoparticles was in the oxidation state 2+, they can be characterized as maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles. The average particle size, determined from the broadening of the diffraction peaks, was found to be 13 nm, agreeing well with the size $13.7 \pm 2.9 \text{ nm}$ estimated from the TEM images (figure 2). The saturation magnetization of the as-synthesized nanoparticles was determined as 68 emu g^{-1} .

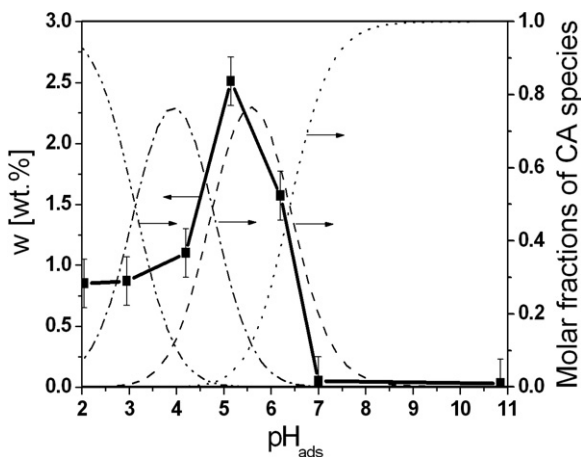


Figure 4. The content of dispersed nanoparticles in the stable suspension (w) (—) as a function of pH value applied during the adsorption of CA (pH_{ads}) at a temperature (T_{ads}) of 80°C . The total concentration of citric acid in solution applied during the adsorption step was $\gamma(\text{CA}) = 0.02 \text{ g ml}^{-1}$. The CA-coated nanoparticles were suspended at $\text{pH}_{\text{susp}} = 10.1$. The changing of w is superimposed on the calculated curves, showing the relative fraction of individual CA species as a function of pH (marked in the graph with H_3A (— · — · —), H_2A^- (— · — · —), HA^{2-} (— · — · —), A^{3-} (· · · · ·)) for undissociated, singly dissociated, doubly dissociated and fully dissociated CA, respectively).

In order to introduce the nanoparticles into a stable water suspension, CA was adsorbed onto their surfaces. Figure 3 shows the changing of the ζ potential with pH value for the as-synthesized nanoparticles and the CA-adsorbed nanoparticles. With the adsorption of CA on the nanoparticles, the isoelectric point (IOP) is shifted from the neutral pH region to a strongly acidic value, below $\text{pH} = 2$. The negative ζ potential of the nanoparticles coated with citric acid is thus already high in the neutral region of pH and much higher than that of the as-synthesized nanoparticles in the basic pH region. These results suggest that besides a minor steric effect, the main repulsive forces between the CA-coated nanoparticles in the water suspension originate from an electrostatic contribution, even at neutral pH.

Figure 4 shows the changing of the content of nanoparticles in a stable suspension (w) as a function of the pH value applied during the adsorption step (pH_{ads}). These data are superimposed on the curves showing the fraction of different CA species as a function of pH, calculated using dissociation equilibria. It is evident that the adsorption process is the most efficient when carried out at a pH around $\text{pH}_{\text{ads}} = 5.2$. In the acidic region of pH values the surface of the as-synthesized nanoparticles is positively charged (see figure 3). The positive charge at the surface promotes the bonding of the negatively charged, dissociated citric acid. At pH values around 5.2, the two carboxyl groups of the CA are dissociated. Obviously, the optimal conditions for the preparation of a stable suspension are reached when the CA bonds to the nanoparticle surfaces with two carboxyl groups, leaving one group unbonded. When dissociated, this free carboxyl group can provide a large surface charge in the suspension. According to the calculations of the dissociation equilibria presented in figure 4, all three

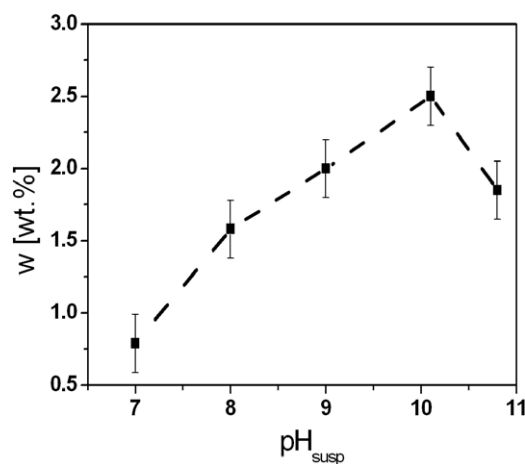


Figure 5. The content of dispersed nanoparticles in the stable suspension (w) as a function of pH value applied during the suspending of the CA-coated nanoparticles (pH_{susp}). CA was adsorbed onto the nanoparticles at $\text{pH}_{\text{ads}} = 5.2$, $\gamma(\text{CA}) = 0.02 \text{ g ml}^{-1}$, and $T_{\text{ads}} = 80^\circ\text{C}$.

carboxyl groups of the CA are dissociated at pH values above 8.

As expected, the stable suspension with the highest w of 2.5 wt% was obtained when the CA was adsorbed onto the nanoparticles at a pH_{ads} of 5.2 and then the particles were suspended at a pH_{susp} of 10.2 (figure 5). At lower pH values the value of w decreased due to the lower ζ potential; however, even at a neutral pH of 7, approximately 0.8 wt% of the nanoparticles remained in the suspension. The w value also decreased at pH values above $\text{pH}_{\text{susp}} = 10.2$, most probably because the ζ potential decreases due to the compression of the double layer at the surface with increased ionic strength caused by the hydroxide addition.

The preparation of a stable suspension was not successful when the CA was adsorbed at pH_{ads} values below approximately 4.5, where only one carboxyl group of the CA is dissociated. At those low pH values the nanoparticles started to dissolve in the aqueous solution of singly dissociated CA. A chemical analysis of the solutions showed a strong increase in the amount of dissolved Fe ions below a pH of approximately 5.

Apart from the pH_{ads} value the process of CA adsorption also depends strongly on the total concentration of CA dissolved in the solution during the adsorption step. The amount of CA adsorbed on the nanoparticles is in equilibrium with the CA dissolved in the aqueous medium. Thus, it is expected that the amount of adsorbed CA would increase in parallel with the increasing concentration of dissolved CA. Figure 6 shows the changing of the value of w as a function of the total CA concentration in the solution applied during the adsorption step ($\gamma(\text{CA})$). As expected, the value of w increases with the increasing $\gamma(\text{CA})$ to reach an optimal value of approximately 0.02 g ml^{-1} . At higher $\gamma(\text{CA})$, the value of w started to decrease because of the decrease in the ζ potential due to the high ionic strength of the dissolved CA.

The influence of the temperature applied during the adsorption process (T_{ads}) on the content of nanoparticles in the

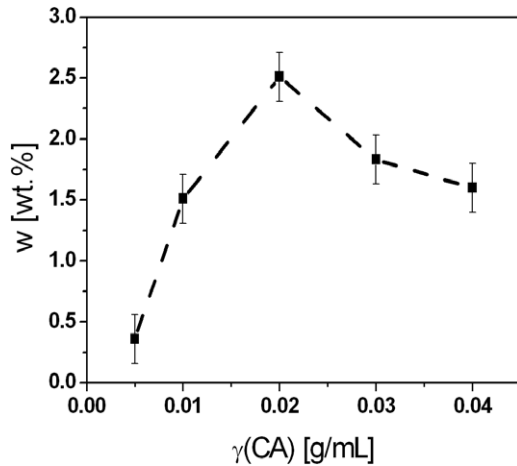


Figure 6. The content of dispersed nanoparticles in the stable suspension (w) as a function of total concentration of CA ($\gamma(\text{CA})$) in the solution applied during the adsorption process at $\text{pH}_{\text{ads}} = 5.2$ and $T_{\text{ads}} = 80^\circ\text{C}$. The CA-coated nanoparticles were suspended at $\text{pH}_{\text{susp}} = 10.1$.

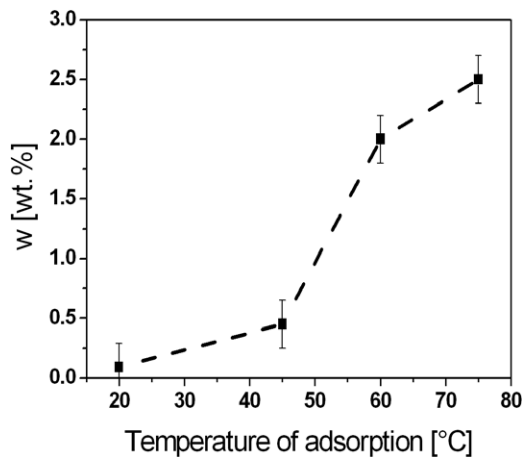


Figure 7. The content of dispersed nanoparticles in the stable suspension (w) as a function of temperature applied during the adsorption process (T_{ads}) at $\text{pH}_{\text{ads}} = 5.2$ and $\gamma(\text{CA}) = 0.02 \text{ g ml}^{-1}$. The CA-coated nanoparticles were suspended at $\text{pH}_{\text{susp}} = 10.1$.

stable suspension is illustrated in figure 7. The value of w increased with the applied temperature. Higher temperatures help in the adsorption process by increasing the concentration of dissociated CA and probably by promoting the bonding of CA to the surfaces of the nanoparticles.

The ferrofluid with the highest content of magnetic nanoparticles ($w = 2.5\%$) prepared by the adsorption of CA onto the nanoparticles at $T_{\text{ads}} = 80^\circ\text{C}$, $\text{pH}_{\text{ads}} = 5.2$, and $\gamma(\text{CA}) = 0.02 \text{ g ml}^{-1}$ and their suspension at $\text{pH}_{\text{susp}} = 10.1$ were characterized using magnetic measurements. The saturated volume magnetization of the ferrofluid reached 1.4 mT (figure 8). The measurement of the temperature dependence of the magnetization under zero-field cooling (ZFC) and cooling in a low magnetic field of 100 Oe (FC) (figure 9) revealed the superparamagnetic nature of the material. The two curves split at a temperature of approximately 100 K, while the ZFC curve shows a

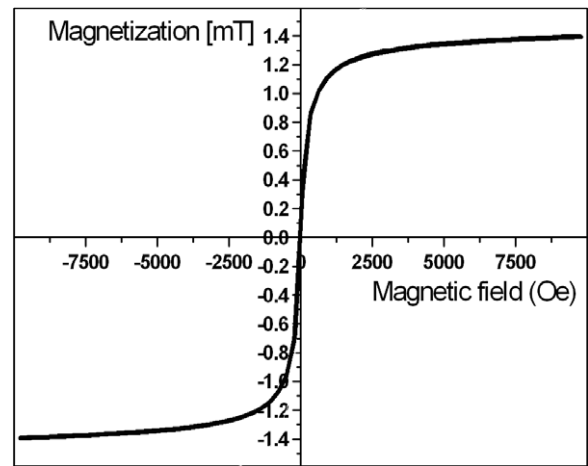


Figure 8. The magnetic measurements of ferrofluid prepared at $\text{pH}_{\text{ads}} = 5.2$, $\gamma(\text{CA}) = 0.02 \text{ g ml}^{-1}$ and $T_{\text{ads}} = 80^\circ\text{C}$. The CA-coated nanoparticles were suspended at $\text{pH}_{\text{susp}} = 10.1$.

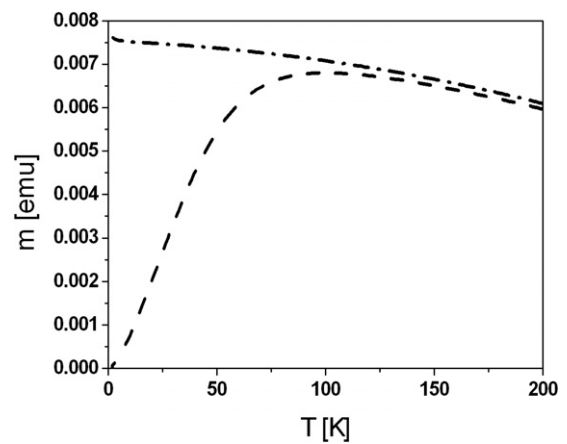


Figure 9. Zero-field (---) and field cooling (— · —) measurements of ferrofluid prepared at $\text{pH}_{\text{ads}} = 5.2$, $\gamma(\text{CA}) = 0.02 \text{ g ml}^{-1}$ and $T_{\text{ads}} = 80^\circ\text{C}$. The CA-coated nanoparticles were suspended at $\text{pH}_{\text{susp}} = 10.1$.

broad maximum, suggesting a blocking temperature (T_B) of approximately 90 K.

4. Conclusion

Stable suspensions of magnetic iron oxide nanoparticles in water (water-based ferrofluid) were prepared using citric acid (CA) as a surfactant. The influences of different factors on the content of the nanoparticles in the stable suspension were systematically studied. The adsorption of CA onto the nanoparticles is the most effective at pH values around 5.2, where two carboxyl groups of CA are dissociated, whereas the highest content of the CA-coated nanoparticles is suspended in water at a pH of around 10, where the citric acid is fully dissociated. The content of nanoparticles in the finally prepared ferrofluid is also influenced by the temperature and the total CA concentration applied during the adsorption of the CA onto the nanoparticles.

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