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Synthesis and properties of Mn-Zn ferrite ferrofluids

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A Mn-Zn ferrite ferrofluid is produced by chemical synthesis. Two different types of ferrofluids, according to the type of carrier liquid, are synthesized: an aqueous cationic ferrofluid and a surfacted hydrocarbon-based one. Ferrite particles are characterized by using several techniques: X-ray diffraction, transmission electronic microscopy, IR-spectroscopy, thermogravimetry, magnetization measurements and chemical analysis. Particles size depends on the synthesis parameters and can be partly controlled by choosing the type of the coprecipitating base. Increasing of the Zn concentration leads to smaller size of synthesized particles, as well as effects the content of associated water. Magnetization of the ferrofluid significantly decreases when the degree of Zn substitution exceeds 0.5. © *1999 Kluwer Academic Publishers*

1. Introduction

Ferrofluids are stable colloidal suspensions of ultrafine magnetic particles dispersed in liquid. They retain the properties of a fluid even in the presence of high magnetic fields and particles do not separate from the carrier liquid. Union of both fluid and magnetic properties makes them useful for numerous industrial applications. Mn-Zn mixed ferrites are chosen here according to their high sensitivity of magnetization to temperature. Ferrofluids constituted by these ferrites may be good candidates for liquid carriers in heat-exchange devices using magnetocaloric energy conversion [1, 2].

According to the method of colloidal stabilization two main types of ferrofluids are known: water-based ionic ferrofluids and surfacted organic media based ferrofluids. An easy and convenient chemical synthesis of ionic ferrofluids was proposed by Massart in the early 80s: fine particles are precipitated and then peptized using an appropriate particle surface treatment [3]. Ionic ferrofluids may be used as precursors for a wide class of surfacted ferrofluids. Surfacted ferrofluids, based on low-evaporating non-polar liquids, keep their fluid properties over a rather wide temperature range that is important for practical applications [1, 2]. This paper presents details of a preparation process for fabrication of both ionic and surfacted ferrofluids, as well as investigation of some physical and chemical properties of colloidal ferrite particles with different degrees of Zn substitution.

2. Experimental methods

Samples are examined by chemical analysis, X-rays diffraction, transmission electron microscopy (TEM), IR-spectroscopy, thermogravimetry and magnetisation measurements on vibration sample magnetometer (VSM).

The iron content is determined by chemical titration with ethylendiaminetetraacetic acid (EDTA), while manganese and zinc content is measured by means of flame spectroscopy microanalysis.

X-ray powder diffraction using a CoK_α source is applied for identification of crystalline structure and estimation mean particle size. The estimation is made via the Scherrer formula using the half-maximum width of the (311) X-ray diffraction line [4].

The morphological properties of specimens are observed by TEM. For some samples an estimation of lower and upper particle size limit is made. Magnetization curves of samples are measured by a VSM in fields up to of 10.5 kOe.

Quantity of associated water may serve as an important parameter which may indicate (together with results of X-rays diffraction and magnetic measurements) the extent of crystallization in the particles. Associated water content is estimated by thermogravimetry and by calculation. Samples are previously washed with acetone and ether and then dried at room temperature. Thermogravimetrical (TG) measurements are performed using a Perkin-Elmer TG-Analyser up to 750 °C in an inert gas atmosphere. The TG heating rate is 5–10 °C/min. Weight of the sample is continuously monitored during the heating process. The difference in weight measured at 750 and 20 °C is considered as an estimate of the content of water retained in the particles.

Estimation of water content by calculation is made on the assumption that chemical composition of particles may be described by the following formula

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$\{(Mn_aZn_bO_{a+b})(Fe_cO_{3c/2})\}(nH_2O)$, where $a + b + c = 3$, and thus mass attributed to oxygen may be calculated knowing the content of metals from the chemical analysis. Comparing the mass of ferrite corresponding to the part of formula in the brackets { } with directly measured weight of powder gives the difference attributed to the quantity of associated water.

IR spectra in the wave length range of 4000–200 cm^{-1} are performed for samples in the form of dried powders. Sample is mixed with KBr in the proportion 1 : 30 and a thin pellet is formed by pressing.

3. Chemical synthesis of ferrofluid

3.1. Introduction

Preparation of ferrofluids requires a fine particle synthesis and then the formation of stable colloidal solution. Magnetic particles must be chemically stable in the liquid carrier and have a convenient size to provide colloidally stable ferrofluid. For Mn and Co ferrites, suitable particle sizes must not exceed 11–12 nm [5]. As Mn-Zn ferrite has approximately the same specific gravity as Mn and Co ferrites ($\sim$5 g/cm^3), this size range is transferable to the Mn-Zn ferrite particles. Synthesis of ultrafine Mn-Zn ferrite particles with size in the range 6–20 nm by chemical coprecipitation method is already known [6, 7]. However, control of Mn-Zn ferrite nanoparticles size by variation of synthesis conditions still remains a serious problem. There is also little published information on preparation of Mn-Zn ferrite ferrofluids [1, 8–10]. Preparation of ionic ferrofluid with Mn-Zn ferrite particles has not yet been performed. The preparation of both ionic water-based and surfacted hydrocarbon-based Mn-Zn ferrite ferrofluid is described below.

Ultrafine Mn-Zn ferrite particles are obtained via chemical *coprecipitation and ferritization*. These are two sequential processes that include coprecipitation of metal salts into hydroxides, which occurs immediately, followed by transformation of hydroxides into ferrite, which starts at coprecipitation but requires certain time and heating to complete [6, 7]. Samples after coprecipitation and ferritization are further named ‘coprecipitated and heated’.

For an ionic ferrofluid formation of a stable colloidal solution is realized by *surface treatment and stabilization* [5]. This involves coating particles with a suitable surface charge density to prevent agglomeration. Henceforth samples are named ‘surface treated’ and designated with letter ‘f’.

For surfacted ferrofluids in a non polar media, a stable colloidal solution is obtained in two different ways:

(1) surfactation of particles after coprecipitation and heating stage and transferring them into nonpolar media;

(2) surfactation of particles at the stage of precursor ionic ferrofluid and transferring them into nonpolar media.

3.2. Coprecipitation and ferrite formation

3.2.1. General conditions

Mn-Zn ferrite particles are prepared by coprecipitation of aqueous solutions of $MnCl_2$, $ZnCl_2$ and $FeCl_3$ mixtures in an alkaline medium. Initial molar proportion ([Mn] + [Zn])/[Fe] is always taken as the stoichiometric 1/2. Initial concentration of salts is taken 0.12 mol/l of total metal content Me ([Me] = [Fe] + [Mn] + [Zn]).

Three different bases are taken as coprecipitating agents: sodium hydroxide (NaOH), methylamine (CH_3NH_2) and ammonia (NH_3). For NaOH, the reaction time is usually 40 min (if not specially mentioned), for CH_3NH_2 and NH_3 the reaction time are 30 and 10 min respectively. Formation of Mn-Zn ferrite particles requires the heating of the solution at elevated temperatures [6, 7]. For coprecipitation with NaOH, conditions close to boiling are preferrable. For CH_3NH_2 and NH_3, reaction temperatures may not exceed 90 and 60 °C, respectively, due to high evaporation of these bases.

3.2.2. Zn substitution degree

Compositions with different initial degrees of Zn substitution x_0 $[Mn^{2+}]_{1-x_0}$ $[Zn^{2+}]_{x_0}$ $[Fe^{3+}]_{2.0}$, where x_0 is 0; 0.2; 0.4; 0.5; 0.6; 0.8; 1.0, are taken for initial mixtures of metal salts. For NaOH and CH_3NH_2, it is found that increased x_0 leads to formation of particles of smaller sizes. Mean sizes of particles determined by the Scherrer formula from X-ray powder diffraction data are summarized in Table I, and shown schematically in Fig. 1. Mean size of Mn-ferrite particles ($x_0 = 0$) exceeds that of Zn ferrite ($x_0 = 1$) by a factor of $\sim$3 (coprecipitation with NaOH). Mn ferrite particles, coprecipitated with NaOH have mean size $\sim$19 nm (samples A1-A1f) and are too large to form a colloidally stable ferrofluid.

Chemical compositions of coprecipitated particles are found to be close to the initial chemical compositions of the mixtures of metal salts (see Table II and Fig. 5).

Increasing the degree of Zn substitution effects the content of associated water in the particles. Associated

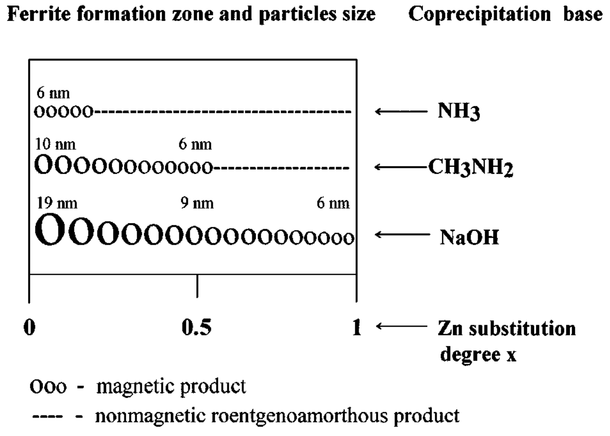

Figure 1 Zones of initial Zn substitution degree x_0 for obtaining ferrite particles with three different coprecipitation bases: NaOH, CH_3NH_2 and NH_3. Size of circles corresponds to mean size of particles, determined by Scherrer formula from X-rays diffraction data.

TABLE I Mean sizes of particles D_{XR} obtained by the Scherrer formula from X-rays powder diffraction. D_{XR} values are shown for coprecipitated and heated in an alkaline solution particles as well as for particles subjected to additional surface treatment

	Coprecipitation base							
	NaOH				CH_3NH_2			
	Sample after coprecipitation and heating in an alkaline solution		Sample after surface treatment (steps 3.3.1 and 3.3.2)		Sample after coprecipitation and heating in an alkaline solution		Sample after surface treatment (steps 3.3.1 and 3.3.2)	
Zn-substitution degree (initial)x_0	Name	D_{XR} (nm)	Name	D_{XR} (nm)	Name	D_{XR} (nm)	Name	D_{XR} (nm)
0.0	A1	18.8	A1f	19.0	A2	9.9	A2f	10.0
0.2	B1	11.0	B1f	11.4	B2	6.8	B2f	7.6
0.4	C1	9.9	C1f	10.4				
0.5	D1	8.6	D1f	8.8	D2	6.0	D2f	7.0
0.6	E1	7.3	E1f	7.6				
0.8	G1	6.6	G1f	6.0				
1.0	J1	6.2	J1f	5.9				

TABLE II Chemical composition of particles coprecipitated and heated in alkaline solution. Initial chemical composition of a reacting mixture: $[Mn^{2+}] = 50(1 - x_0)$, $[Zn^{2+}] = 50x_0$, $2[Fe^{3+}] = 50$ in mol %, where x_0 is the initial Zn substitution degree

Initial mixture of reagents	Sample after coprecipitation and heating				
		Metal content (mol %)			
Zn substitution degree x_0	Name of sample	MnO	ZnO	Fe_2O_3	Zn substitution degree x
0.20	B1	39.0	10.0	51.0	0.20
0.40	C1	29.5	19.5	51.0	0.40
0.50	D1	24.5	22.0	53.5	0.47
0.60	E1	20.0	27.5	52.5	0.58
0.80	G1	10.5	37.5	52.0	0.78
0	A2	50.9	0.0	49.1	0.0
0.20	B2	41.2	7.7	51.1	0.16
0.50	D2	26.1	22.3	51.6	0.46

TABLE III The associated water content in particles coprecipitated and heated in alkaline solution. Data for samples with different Zn substitution degree x coprecipitated with two different bases NaOH or CH_2NH_3 are presented. Water content is determined by thermogravimetry (TG) and by calculation from metals content

			Content of associated water (w %)	
Name of Sample	Coprecipitation base	Zn substitution degree x	TG	Calculation
A1	NaOH	0	3.4	6.0
C1	NaOH	0.40	4.5	5.6
D1	NaOH	0.47	9.5	10.0
E1	NaOH	0.58	10.1	10.6
G1	NaOH	0.78	12.0	12.7
A2	CH_2NH_3	0	6.0	6.5
D2	CH_2NH_3	0.47	10.0	13.9

water content in particles grows with increasing Zn substitution x (see Table III). This agrees with observations in [6] and may be related to the higher affinity of Zn with respect to water. Reduction in the particle size with increasing x must also be taken into account.

3.2.3. Nature of the coprecipitating base

Three different bases are used as coprecipitating agents: NaOH, CH_3NH_2 and NH_3. In the case of NaOH, concentration of the base is ~0.4 mol/l and provides a pH = 12.5–13 after coprecipitation. For the two other bases, CH_3NH_2 and NH_3, concentration of the base is 0.8–1 mol/l and pH after coprecipitation is 10.5–11 and 9.5, respectively. The nature of the coprecipitating base has a significant influence on the size of the ferrite particles. For Mn-ferrite, it is shown that three bases result in particles with decreasing size in the following sequence: $D_{NaOH} > D_{CH_3NH_2} > D_{NH_3}$ [5]. For Mn-Zn ferrite, the same trend holds (see Table I and Fig. 1). Coprecipitation with NaOH leads to the formation of ferrite for the entire range of x_0 (see Table I and Fig. 1). For CH_3NH_2 and NH_3, formation of ferrite particles takes place only within a limited range of x_0 (see Fig. 1). When the initial Zn substitution exceeds a definite threshold, a nonmagnetic roentgenamorphous product is obtained. This may be due to formation of soluble complexes of Zn^{2+} and partly Mn^{2+} by NH_3 and CH_3NH_2 [11]. Formation of an amorphous precipitate was also reported for the case of Fe^{3+} and Zn^{2+} coprecipitated with NH_3 and heated at 60 °C for several hours [12]. Ferrite particles obtained under boundary conditions of ferrite formation zones (for example, sample D2 at $x_0 = 0.5$, coprecipitated with CH_3NH_2) demonstrate a reduced resistance to acid attack.

3.2.4. Duration of heating after coprecipitation

The formation reaction of Mn-Zn ferrite requires certain conditions, which depend mainly on temperature and pH [6]. The influence of heating time on the properties of resulting particles is studied for samples coprecipitated by NaOH with an initial Zn substitution of $x_0 = 0.5$. Samples are boiled for different times at 95–100 °C in a precipitation solution (pH ~ 12.5) under vigorous stirring. No any significant changes in the chemical composition of particles are found in the process of boiling (see Table IV).

X-rays powder diffraction diagrams for 1, 20 and 90 min boiled samples demonstrate evolution of ferrite crystalline structure (see Fig. 2). Particles after 1 min of boiling show hardly pronounsed widened peaks of spinel structure, whereas already after 20 min of boiling these peaks become well pronounced. Mean sizes D_{XR}, estimated from X-rays powder diffraction and

TABLE IV Properties of particles heated in alkaline solution for different time periods after coprecipitation with NaOH. Chemical composition, content of associated water in the particles (determined by thermogravimetry (TG) and calculated), particles mean size D_{XR}, obtained from X-rays powder diffraction by the Scherrer formula and size limits from transmission electronic microscopy D_{TEM}

Time of heating (min)	Content of metals (mol %)			Content of associated water (w %)		D_{XR} (nm)	D_{TEM} (nm)
	MnO	ZnO	Fe_2O_3	TG	Calculated		
1	23.3	22.2	54.5	23.7	22.0	4.9	2.0–4.0
20	24.0	23.3	52.7	10.3	9.8	9.0	2.5–9.5
40	23.1	23.3	53.6	11.5	11.8	8.2	3.0–10.0
90	24.0	23.3	52.7	10.4	12.5	8.6	5.0–10.0

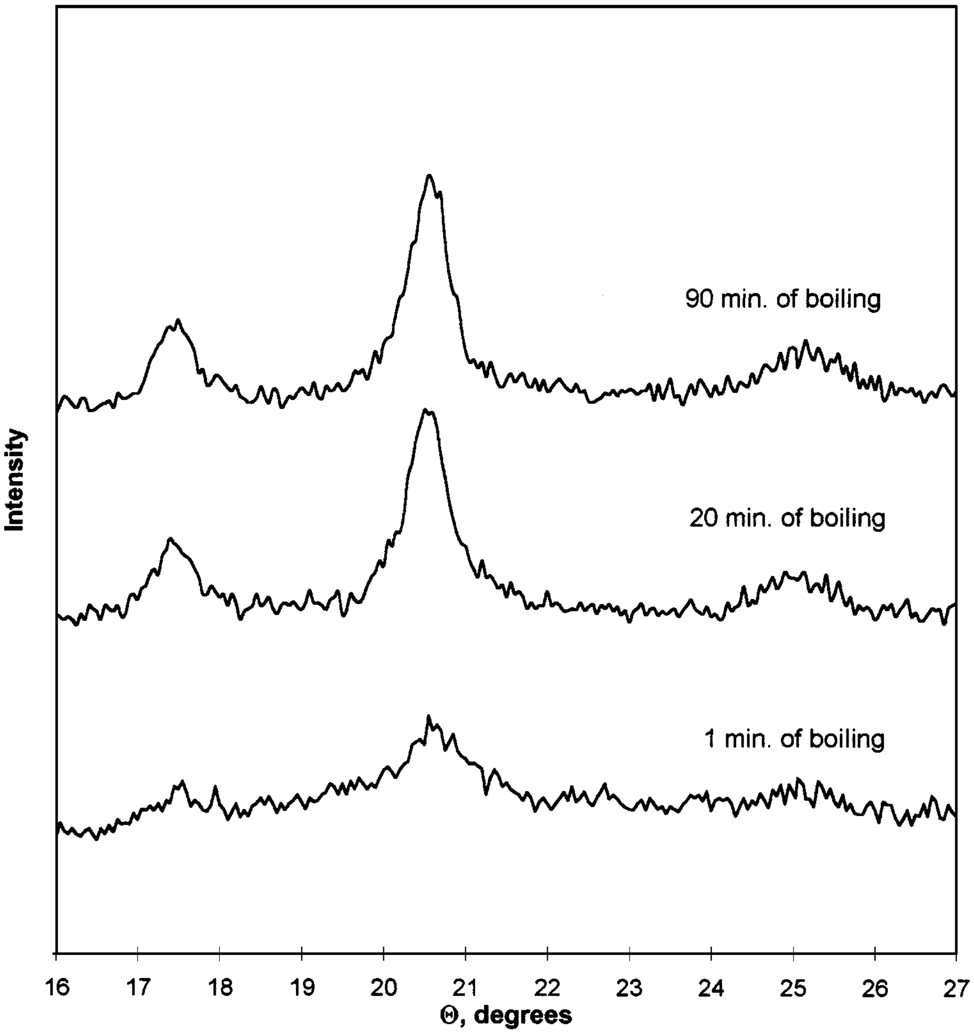

Figure 2 X-rays diffraction powder diagrams for coprecipitated particles boiled in an alkaline solution for different times.

size limits estimations D_{EM} made from electronic microscopy pictures show that significant growth of particle size occurs in the first 20 min (see Table IV). It is notable, that D_{XR} is near upper limit of D_{EM}.

Associated water content in particles is found to significantly decrease in the first 20 min. Thermogravimetric curves for 1 and 20 min heated samples are shown in Fig. 3. For 20 min boiled particles evaporation of about 70% of the associated water takes place in the temperature range of 20–200 °C, whereas the remaining 30% evaporates at higher temperatures (up to 750 °C).

Further heating of precipitate in an alkaline solution at 100 °C for up to 90 min fails to change the associated water content within the particles.

The IR spectroscopy of samples heated for different time periods allows one to follow the process of ferrite formation and decrease in water content of the particles [13]. The IR-spectra of coprecipitated samples heated for 1 and 20 min are shown in Fig. 4. The sample heated for 1 min fails to demonstrate well resolved absorption wavebands at 580 and 460 cm^{-1}, which correspond to metal-oxygen bonds and are considered confirmation of the existence of the ferrite phase [13, 14]. After 20 min of heating these wavebands become much more intense, while adsorption at 3400–3440 cm^{-1}, which corresponds to the associated water decreases. Heating up to 90 min leads to formation of additional adsorption band at 900 cm^{-1}.

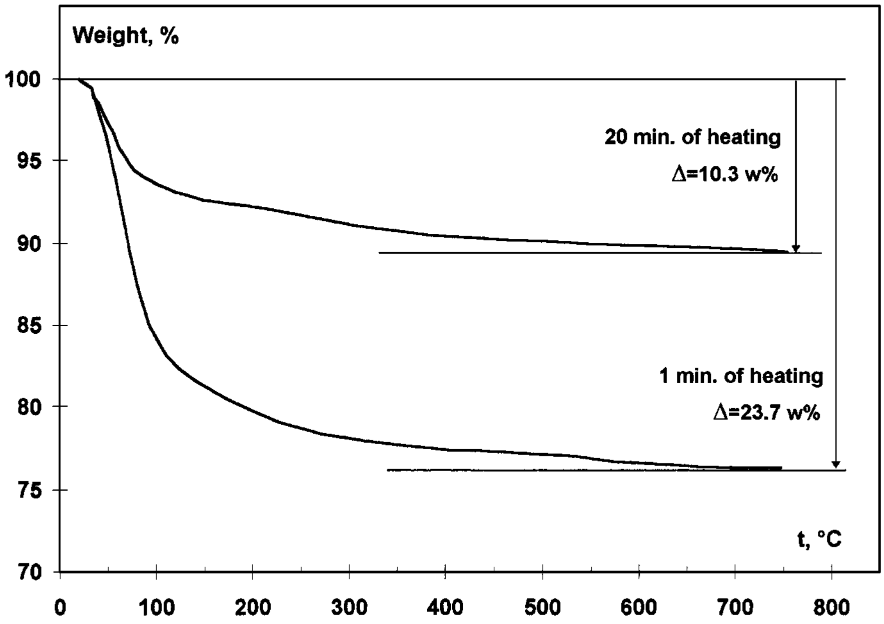

Figure 3 Thermogravimetrical curves (relative weight versus temperature) for coprecipitated samples boiled in an alkaline precipitation solution for different times.

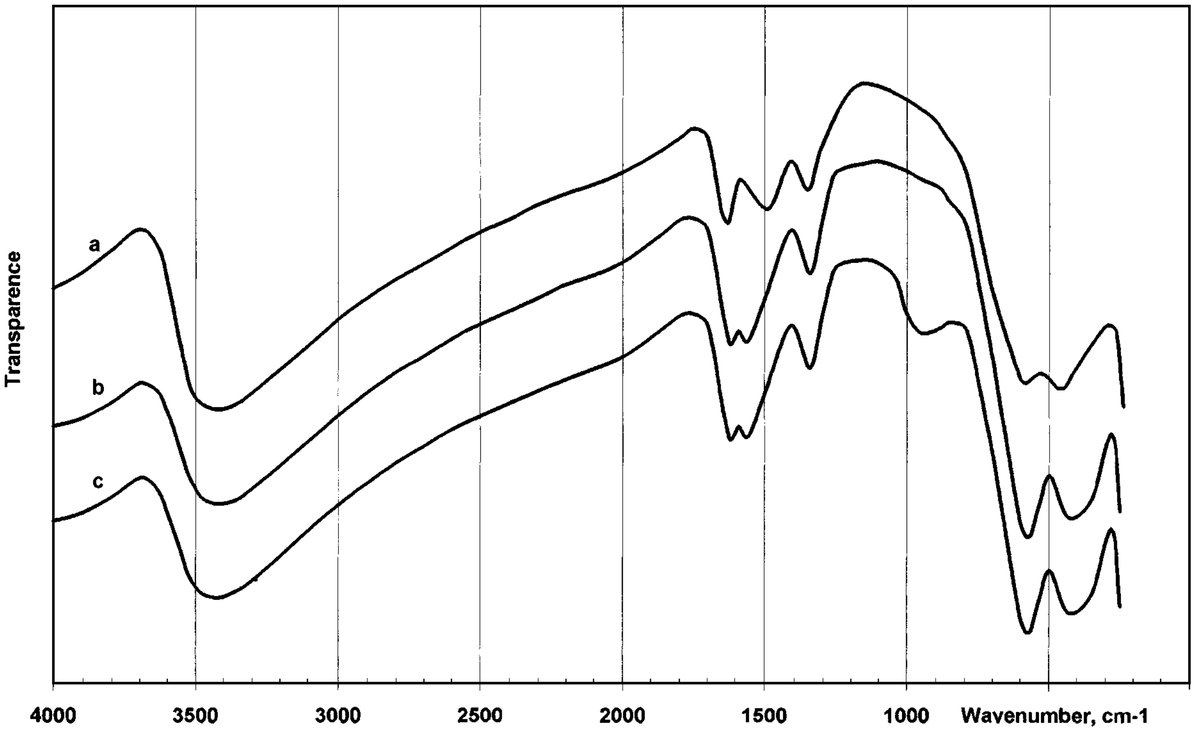

Figure 4 IR-spectra of coprecipitated samples boiled in an alkaline precipitation solution for different times: (a) for 1 min, (b) for 20 min, and (c) for 90 min.

3.3. Surface treatment: formation of cationic water-based ferrofluid

To obtain a stable water-based ferrofluid, it is necessary to provide sufficient electrostatic repulsion between the particles. Surface treatment and stabilization procedures developed for Mn and Co ferrite fine particles [5], are applied for the preparation of Mn-Zn ferrite ionic ferrofluid. These include two steps, namely, acid treatment of the surface of particles (treatment with nitric acid HNO_3), and surface stabilization (treatment with $Fe(NO_3)_3$).

3.3.1. Acid surface treatment

Due to absorption of hydroxyl anions OH^-, ferrite particles obtained after coprecipitation and heating bear negative surface charge even after washing with distilled water. Counterions from coprecipitation bases (Na^+, $CH_2NH_3^+$ or NH_4^+) exhibit the screening effect and do not achieve sufficient repulsion between particles [3]. Massart has shown that these counterions may be replaced by low-polarizing anions (NO_3^-), hence, a colloidally stable cationic ferrofluid in an acidic medium (cationic ferrofluid) may be obtained [3]. This

TABLE V Chemical composition of particles before and after surface treatment: Zn substitution degree $x (x = [\mathrm{Zn}]/([\mathrm{Zn}] + [\mathrm{Mn}]))$ and molar ratio $X (X = ([\mathrm{Zn}] + [\mathrm{Mn}])/[\mathrm{Me}]$, where Me is the total metal content $[\mathrm{Me}] = [\mathrm{Fe}] + [\mathrm{Mn}] + [\mathrm{Zn}])$

Coprecipitated and heated particles (before step 3.3.1)			Surface treated particles (after subsequent steps 3.3.1 and 3.3.2)		
Name of sample	Zn substitution degree x	Molar ratio X	Name of sample	Zn substitution degree x	Molar ratio X
B1	0.20	0.32	B1f	0.24	0.24
C1	0.40	0.32	C1f	0.47	0.25
D1	0.47	0.30	D1f	0.53	0.24
E1	0.58	0.31	E1f	0.62	0.24
G1	0.78	0.32	G1f	0.79	0.24
B2	0.16	0.32	B2f	0.21	0.23
D2	0.46	0.32	D2f	0.56	0.20

replacement is realized by exposing the primary alkaline precipitate to a 2 mol/l HNO_3 solution [5]. The surface of particles is acidified and positively charged.

At the same time, partial dissolution of the particles during acid treatment is observed. For example, 25 min acid exposure leads to dissolution of 10–20 wt % of precipitate. Chemical analysis of particles and of acid solutions after acid treatment demonstrates that Mn, Zn and Fe dissolve from particles differently. Mn and Zn dissolve relatively to a greater extent than Fe, whereas the dissolution of Mn is more pronounced than that of Zn (see Table V). Therefore, the degree of Zn-substitution x in particles after acid treatment may change (usually increases slightly).

It must be noted that cationic particles are flocculated with an excess of HNO_3. A cationic ferrofluid may be obtained at pH ~ 2 by addition of distilled water.

3.3.2. Surface stabilization of particles: Fe(NO$_3$)$_3$ treatment procedure

Cationic ferrofluids obtained directly from acid-treated ferrite particles are not chemically stable with time. Gradual dissolution of particles in acid media (pH ~ 2—conditions of cationic sol) and gelation of solution takes place. To prevent this a chemically inactive layer on the particles surface is created by ferric nitrate treatment known to be effective for Mn and Co ferrite particles [5]. After HNO_3 surface treatment the precipitate is added to a ferric nitrate solution of 0.3 mol/l concentration and kept boiling for half an hour.

After acidic, and subsequent ferric nitrate treatments, the molar ratio X $(X = ([\mathrm{Mn}] + [\mathrm{Zn}])/[\mathrm{Me}])$ decreases from the stoichiometric value of 0.33 to 0.20–0.25. In other words, the molar part of Fe significantly increases (see Table V). Similar changes in the chemical composition are reported for the same surface treatment of Co and Mn ferrite particles [5]. Changes of chemical composition of particles after surface treatment procedures are also demonstrated in the ternary diagram (see Fig. 5). Composition of particles after coprecipitation and heating in an alkaline solution are taken as initial points and that of particles of cationic ferrofluids as final points.

Surface treatment procedures lead to a slight increase in the mean particle size of particles (see Table I). This may be related to the dissolution of the predominantly small-size particles of the polydispersed sample during the process of acid treatment.

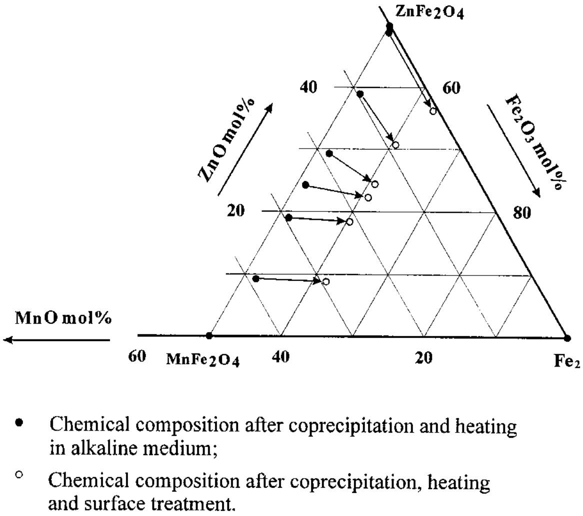

Figure 5 The ternary diagram showing chemical compositions of coprecipitated and heated particles and of cationic ferrofluids synthesized at different initial Zn substitution degrees (coprecipitation with NaOH).

3.4. Formation of surfacted hydrocarbon-based ferrofluid

In order to peptize particles in non-polar media, the particles are coated with surfactant chains. In order to stick to the particle surface, the surfactant must have a lipophilic tail with an affinity to the solvent and a polar head. In our case, the polar carboxilate group of oleic acid is complexing with superficial metal and clings to the surface of the particle in the alkaline medium [15]. After surfactation, particles leave the aqueous medium and concentrate in the non-polar one. In such a way it is possible to peptize in non-polar medium particles obtained directly after coprecipitation, as well as particles initially obtained as ionic ones (through surface treatment). In the present paper, both techniques are used and properties of finally produced ferrofluids are compared. A relatively low-evaporating hydrocarbon dodecane $C_{12}H_{26}$ is considered as a suitable non-polar carrier liquid.

3.4.1. Direct surfactation of coprecipitated particles (surfacted ferrofluid type 1)

A surfacted ferrofluids of type 1 is prepared by the following procedure: surfactant (oleic acid) diluted in dodecane at a concentration of about 12 vol % is added to the wet precipitate (obtained after coprecipitation and

TABLE VI Chemical composition and mean sizes of particles (from X-rays diffraction data) for surfacted ferrofluids prepared by two methods: starting from coprecipitated and heated particles or from cationic (surface treated) particles

Sample	Mean size of particles D_{XR} (nm)	Chemical composition (mol %)		
		MnO	ZnO	Fe_2O_3
Initial mixture of salts	—	25	25	50
Coprecipitated and heated particles (precursor for SF1)	8.5	24.8	24.5	50.7
Surfacted ferrofluid 1 (SF1)	8.3	24.7	24.9	50.4
Cationic ferrofluid (precursor for SF2)	8.8	18.8	22.4	58.8
Surfacted ferrofluid 2 (SF2)	8.9	18.7	22.3	59.0

heating) and the resulting mixture is stirred at 30 °C. The following proportion of surfactant to total metal is utilized: 1 mol oleic acid : 8 mol Me. Particles are surfacted and transferred into an organic phase. This phase is separated and then heated to ∼120 °C under stirring in order to remove the remaining water. The excess of surfactant is eliminated by extraction with methanol.

It is noted that chemical composition of particles of surfacted ferrofluid (type 1) is very close to the composition of the coprecipitated and heated particles (see Table VI).

3.4.2. Preparation of type 2 surfacted ferrofluid from cationic precipitate

Particles after surface treatment (cationic precipitate) are transferred into an anionic precipitate by addition of tetramethylammonium hydroxide (TMAOH). Subsequently, particles are surfacted with oleic acid and transferred into a non-polar medium (see Fig. 6).

TMAOH is added to the cationic precipitate in proportion 1 mol TMAOH : 10 mol Me under stirring. After that, surfactant is added in proportion 1 mol oleic acid : 5 mol Me. The mixture is stirred at 30 °C with the excess oleic acid in ferrofluid extracted by methanol.

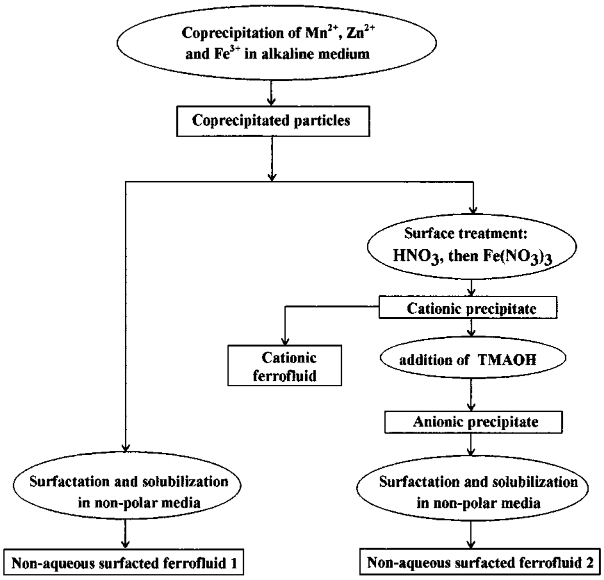

Figure 6 A general scheme of synthesis for surfacted non-aqueous Mn-Zn ferrite ferrofluid. Two pathways are shown: starting directly from coprecipitated and heated particles or from cationic (surface treated) particles.

TABLE VII Specific magnetization σ of cationic ferrofluids with different Zn substitution degree x in magnetic fields of two different strengh: 1 kOe and 10.5 kOe

Zn substitution degree x	σ (emu/g) ($H = 1$ kOe)	σ (emu/g) ($H = 10.5$ kOe)
0.24	31.7	42.0
0.47	33.9	49.0
0.62	13.9	34.6
0.79	3.1	17.5

At the final stage the chemical composition of particles (surfacted ferrofluid 2) is very close to the composition of its precursor cationic ferrofluid (see Table VI).

4. Magnetic characterization

The magnetic characterization is based on measuring the specific magnetization of ferrofluids. Specific dry weight magnetization σ of particles is subsequently calculated using the concentration of metals in the ferrofluid. Mn-Zn ferrite particles with $x > 0.3$ are found to be far from saturation in a magnetic field of 10.5 kOe (maximal available for the magnetometer used) and therefore magnetic saturation magnetization for these samples can not be correctly determined. These limitations must be taken into account considering magnetisation data for samples with different Zn substitution degree x.

Values of specific magnetisation for cationic ferrofluids in magnetic fields of 1 and 10.5 kOe are summarized in Table VII. Maximum magnetization is achieved at $x = 0.47$. Further increase of x leads to a significant decrease in magnetization.

Conclusions

Synthesis procedures of a Mn-Zn ferrite cationic ferrofluid and a surfacted hydrocarbon-based one are described. Ultrafine ferrite particles are obtained by chemical coprecipitation and subsequent heating process in alkaline medium. The most relevant changes during the ferrite formation process take place within the first 20 min of heating. Particles size can be partly controlled by choosing the type of the coprecipitating base. Three bases yield particles with respective sizes decreasing in the following order: $D_{NaOH} > D_{CH_3NH_2} > D_{NH_3}$. Coprecipitation with NaOH leads to formation of ferrite within the entire range of initial Zn substitution x_0, whereas CH_3NH_2 and NH_3 yield ferrites only under the condition that the x_0 does not exceed certain value. Increase in x_0 leads to smaller size of ferrite particles and higher content of associated water.

A cationic ferrofluid is obtained from coprecipitation and subsequent surface treatment of particles with HNO_3 and $Fe(NO_3)_3$. This surface treatment leads to an increase in the relative content of iron in the resulting particles.

For cationic ferrofluids maximum specific magnetization (in magnetic fields $H \leq 10.5$ kOe) is found at Zn substitution $x \sim 0.5$. Further increase of x leads to a significant decrease in magnetization.

Surfacted ferrofluids are prepared by two different ways: directly from coprecipitated and boiled particles or from surface treated (cationic) particles. Chemical composition and mean size of particles of these ferrofluids are very close to those of their respective precursors.

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