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Aqueous ferrofluids based on manganese and cobalt ferrites

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Synthesis of two new aqueous ferrofluids is performed chemically according to Massart's procedure. Manganese and cobalt ferrite magnetic particles are precipitated and treated in order to obtain colloidal sols by creating a charge density on their surface. Such "ionic" ferrofluids can be prepared in an acidic (after a treatment by ferric nitrate) or in an alkaline medium at a concentration as high as 17 mol l^{-1}, i.e. a volumic fraction of 0.26. This result makes these new compounds of great interest.

1. Introduction

Magnetic fluids are of interest in various topics such as fluid dynamics or engineering applications [1]. The principal type of magnetic fluid is a colloidal ferrofluid [2] which consists of finely divided magnetic particles suspended in a continuous medium.

A new chemical synthesis of aqueous ferrofluids was proposed by Massart [3–6] in 1980: fine particles of magnetic oxide are directly precipitated out and then peptized using an appropriate particle surface treatment which brings electric charges onto the surface. These electric charges provided by adsorbed HO^- (or H_3O^+) ions introduce repulsive forces between particles [3–7]. Depending on the counterions, repulsive forces may provide a sufficient energy barrier to prevent aggregation of particles. Such ferrofluids may be considered as "ionic ferrofluids" [7]. First carried out on colloidal magnetite (Fe_3O_4), the procedure was improved by Cabuil and Massart [8] on maghemite (γ-Fe_2O_3). Both oxides have spinel-type structure and a large magnetization value. Among other magnetic oxides of spinel-type structure, $MnFe_2O_4$ and $CoFe_2O_4$ ferrites show also a large magnetization value [9] and then have been chosen in order to obtain new ferrofluids.

This paper presents a preparation process of two new ferrofluids based on manganese and cobalt ferrites. The preparation is carried out according to the principle mentioned above. Experimental conditions have to be determined in order to adapt the principle and to succeed in this new synthesis.

2. Experimental details

2.1. Titrations

Sample composition is controlled by chemical analysis. Fe(III) titration is performed by potassium dichromate [10]; Co(II) is determined by indirect titration with Ce(IV) [11] and Mn(II) by atomic absorption spectrophotometry [12].

2.2. X-ray analysis

Spinel structure of precipitates is identified by X-ray powder diffraction. Diffractograms are recorded on a Philips PW 1130 diffractometer using Co Kα radiation.

2.3. Size determination

2.3.1.

The average particle size D_{RX} is determined by Scherrer's formula using the halfwidth of the (311) X-ray diffraction line. In this way, only the crystalline part of particles is taken into account.

2.3.2.

Particle size is also determined from transmission electron microscopy. Micrographs are performed in the Groupement Régional de Mesures Physiques de l'Université Pierre et Marie Curie de Paris on a T.E.M. JEOL 100 CX 2 apparatus. Fig. 1 shows the spherical morphology of particles. The system is polydisperse. Size distribution is evaluated from 5 pictures per sample (approximately 500 particles) by a semi-automatic computing device [13]. The corresponding experimental histogram is drawn in Fig. 2. A fit is attempted by a mean square method. The full line represents the best fit assuming a log-normal distribution

$$P(D) = \frac{1}{D(2\pi)^{1/2}} \exp\left(-\frac{(\ln D - \ln D_0)^2}{2\sigma^2}\right) \quad (1)$$

where $\ln D_0$ is the mean value of $\ln D$ and σ the standard deviation. The most probable diameter corresponding to the max point is $D_{mp} = D_0 \exp(-\sigma^2)$. In the following text and tables D_{ME} corresponds to D_0 and σ to the standard deviation of the log-normal distribution.

2.4. Magnetic material yield

Changes in magnetic flux are determined by an "extraction method" using an EF3 Magnet Physik fluxmeter integrator. The magnetic induction of 1 T is generated by an electromagnet and measured with a Hall probe coupled to a Walker Scientific Incorporation MG-50 gaussmeter (precision of 1×10^{-4} T).

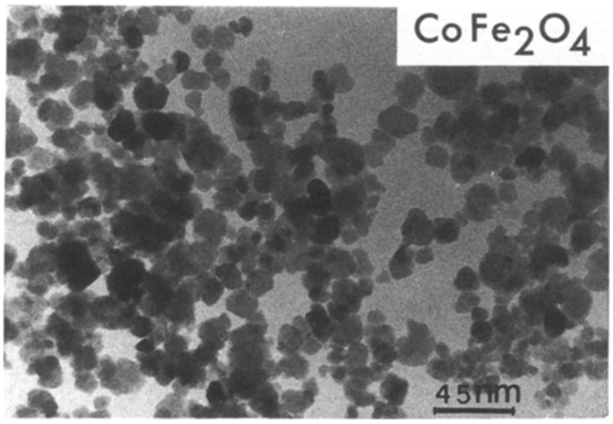

Figure 1 $CoFe_2O_4$ particle sample micrograph.

3. Synthesis

Preparation process of ferrofluids needs two steps: first particle synthesis and secondly preparation of stable colloidal solutions.

Magnetic particles of a ferrofluid must be chemically stable in the liquid carrier and have a convenient size to provide colloidal sols. For magnetite, suitable particle diameters are of the order of a few nanometres. As the manganese and cobalt ferrites have approximately the same specific gravity as magnetite ($\sim 5\,g\,cm^{-3}$), this size range is convenient as well for $MnFe_2O_4$ and $CoFe_2O_4$ particles.

Synthesis of ultrafine manganese and cobalt ferrite particles of diameters ranging from 4 to 15 nm is already known [14–16]. On the contrary, ferrofluid elaboration has not yet been performed with these ferrites. A procedure of ferrofluid preparation is carried out and described below. The general scheme is shown in Fig. 3.

3.1. Coprecipitation (Fig. 3, step 1)

$MnFe_2O_4$ and $CoFe_2O_4$ oxide particles are prepared by coprecipitating aqueous solutions of $MnCl_2$–$FeCl_3$ or $Co(NO_3)_2$–$FeCl_3$ mixtures in alkaline medium. Synthesis does not occur at room temperature and reagents have to be brought to a boil. In order to prevent $FeCl_3$ hydrolysis at this temperature, acid is added to initial mixtures.

Particle sizes are fixed by coprecipitation step. It is therefore necessary to precise experimental conditions in order to get reproducible results.

Parameters acting to a certain extent on this step have then been tested: composition of initial mixtures, composition of the base and operating mode.

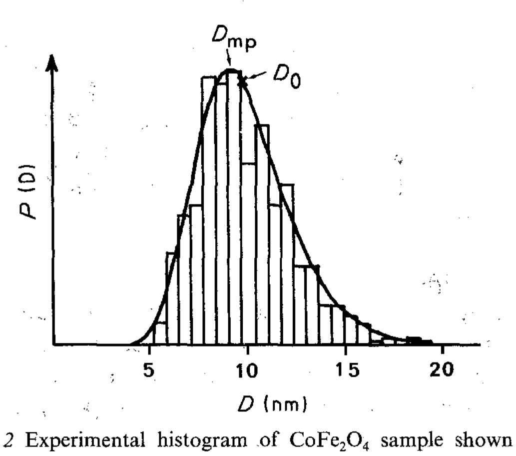

Figure 2 Experimental histogram of $CoFe_2O_4$ sample shown in Fig. 1.

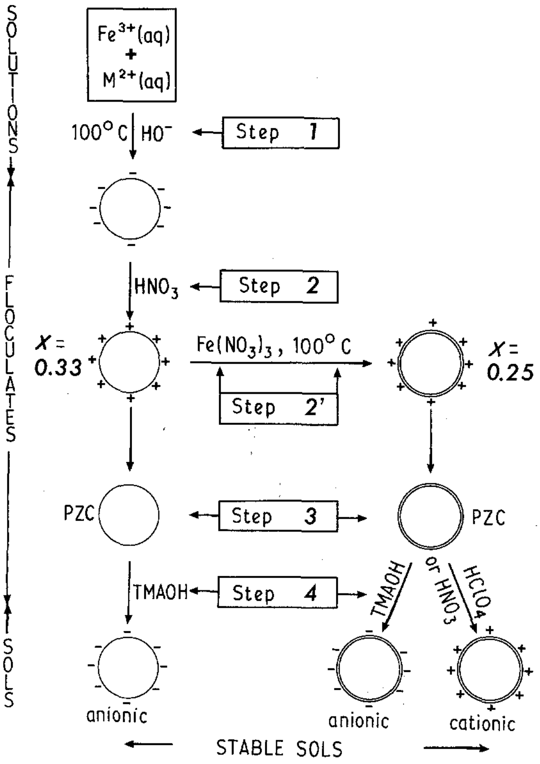

Figure 3 Synthesis general scheme for ferrofluids based on manganese or cobalt ferrites. $M^{2+} = Mn^{2+}$ or Co^{2+}; (aq) = aqueous solution; PZC = point of zero charge; TMAOH = tetramethylammonium hydroxyde.

3.1.1. *Initial molar ratio X_0*

Under varying stoichiometries, magnetic measurements may be used to determine the best initial molar ratio. This molar ratio is expressed by

$$X = \frac{[\mathrm{M(II)}]}{[\mathrm{M(II)} + \mathrm{Fe(III)}]} \quad (2)$$

with M(II) = Mn(II) or Co(II) and X_0 the initial value of X. The expected compounds are magnetizable. Therefore, reaction yields may be compared by magnetic property measurements. Magnetization is proportional to the amount of synthesized material provided that saturation magnetization is reached for all particles: with a magnetic induction of 1 T more than 90% of saturation magnetization is reached with >5 nm γ-Fe_2O_3 particles [17]. Magnetization is proportional to $\Delta\phi$, the magnetic flux variation during a sample extraction from a 1 T magnetic field. Results are plotted as $\Delta\phi = f(X_0)$. Graphs are shown in Fig. 4. The best yield corresponds to the ferrite stoichiometry, that is $X_0 = 0.33$.

TABLE I The influence of the molar ratio X_0 on ferrite particle size

X_0	0	0.20	0.33	0.40	0.60	0.80	1
(1) D_{RX} (nm)	*	13.0	11.0	13.0	11.2	5.0	*
(2) D_{RX} (nm)	*	13.1	13.8	13.1	13.1	*	*

(1) $MnCl_2$–$FeCl_3$ mixture precipitated by CH_3NH_2
(2) Co $(NO_3)_2$–$FeCl_3$ mixture precipitated by NaOH
[Base] = 0.6 mol l^{-1}; n {Fe(III) + M(II)} = 1.5×10^{-2} mol
*No line corresponding to spinel structure on X-ray diagrams.

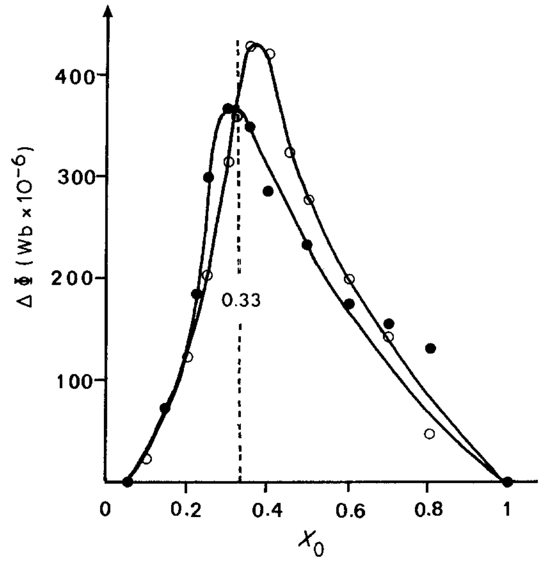

Figure 4 Changes in flux as a function of molar ratio X_0. $FeCl_3$–$MnCl_2$ mixture (●) and $FeCl_3$–$Co(NO_3)_2$ mixture (○). Coprecipitation with (0.6 mol l^{-1}) NaOH. $X_0 = \{[M(II)]/[Fe(III) + M(II)]\}$.

X_0 acts to a certain extent on particle size, for Fe(III)–Mn(II) mixtures. On the contrary, it seems ineffective for Fe(III)–Co(II) mixtures. Results are summarized in Table I.

3.1.2. Acidity of initial mixture

Results on yield are not changed by using H_2SO_4, HNO_3, HCl or $HClO_4$ in order to prevent hydrolysis in the initial mixture. On the contrary, a size effect is noticeable as shown in Table II.

Acid concentration acts also on size and polydispersity. In present syntheses, the range of $[H^+]$ is 0.05 to 0.08 mol l^{-1}.

3.1.3. Influence of the base

The nature of the base acts significantly on the size of ferrites as already shown for magnetite and maghemite. Results for manganese and cobalt ferrites are collected together in Table III.

$MnFe_2O_4$ particles of 16.8 nm D_{RX} diameter precipitated by NaOH cannot provide stable monophasic colloidal sols by further treatment; neither do $CoFe_2O_4$ particles of 2.9 nm D_{RX} diameter precipitated by ammonia.

3.1.4. Operating mode

Reagent addition procedure acts on the particle size, especially the way and the rapidity of reagent mixing. Results reported here in order to get the finest grains are obtained by pouring the base as quickly as possible (about 10 sec) into the M(II)–Fe(III) mixture under vigorous stirring.

As a summary, coprecipitation step performed at 100° C is then largely influenced by several parameters:

(i) Reaction yield depends on initial molar ratio X_0.

(ii) Particle size and polydispersity depend on the operating mode, on the nature of coprecipitating base and on the initial mixture acidity. Control of these parameters allows reproducible results to be obtained.

3.2. Surface treatment (Fig. 3, step 2)

The coprecipitation provides a sluggish precipitate which may be decanted off under magnetic field and washed with water. However, even after washing, counterions from the base play a screening effect and prevent a sufficient repulsion between particles. To suppress the screening effect, it is necessary to wash out base ions: particle surface is cleaned by a (2 mol l^{-1}) HNO_3 solution; it is thereby acidified and positively charged. The NO_3-counterions are non-flocculating ones and it is possible to get a colloidal sol after centrifugation and addition of a minimum amount of water.

As previously shown with colloidal magnetite [3–7], positive charge of surface may be changed into negative one by adding HO^- ions. Provided that counterions are conveniently chosen, an alkaline sol may be prepared. Such alkaline sols are stable. On the contrary, acidic sols prepared directly after step 2 are not chemically stable in time. Manganese and cobalt ferrite particles are progressively destroyed in acidic medium and the sol flocculates. Attempts have then been undertaken to improve the procedure in order to understand acidic attack and to prevent it. Study has been carried out on cobalt ferrite particles.

TABLE II The influence of nature and concentration of acids on ferrite particle size

Acids	Concentration (mol l^{-1})	$MnFe_2O_4$ from (1)			$CoFe_2O_4$ from (2)		
		D_{RX} (nm)	D_{ME} (nm)	σ	D_{RX} (nm)	D_{ME} (nm)	σ
HCl	0	15.6	10.8	0.34	16.8	–	–
	0.017	16.8	13.2	0.20	–	–	–
	0.051	11.7	10.0	0.27	13.8	10.2	0.25
	0.083	11.0	9.7	0.23	13.8	11.2	0.27
	0.296	10.2	10.2	0.20	12.4	–	–
H_2SO_4	0.083	7.6	8.8	0.27	12.4	11.5	0.33
HNO_3	0.083	10.7	10.0	0.25	12.4	–	–
$HClO_4$	0.083	13.0	9.6	0.26	12.4	9.8	0.20

(1) $MnCl_2$–$FeCl_3$ mixture precipitated by CH_3NH_2
$[Mn] = 5 \times 10^{-3}$ mol l^{-1}; $[Fe] = 1 \times 10^{-2}$ mol l^{-1}
$[CH_3NH_2] = 0.6$ mol l^{-1}

(2) $Co(NO_3)_2$–$FeCl_3$ mixture precipitated by NaOH
$[Co] = 5 \times 10^{-3}$ mol l^{-1}; $[Fe] = 1 \times 10^{-2}$ mol l^{-1}
$[NaOH] = 0.6$ mol l^{-1}

TABLE III The size dependence of ferrite particles with regard to coprecipitating base

Base	Concentration ($mol\,l^{-1}$)	$MnFe_2O_4$			$CoFe_2O_4$		
		D_{RX} (nm)	D_{ME} (nm)	σ	D_{RX} (nm)	D_{ME} (nm)	σ
NH_3	0.65	7.3	9.0	0.24	2.9	–	–
CH_3NH_2	0.65	11.0	9.7	0.23	8.3	9.0	0.23
	1.65	12.4	10.7	0.24	–	–	–
NaOH	0.65	16.8	12.3	0.30	13.8	11.2	0.27
	1.65	–	–	–	13.1	10.6	0.34

From initial mixtures with $X_0 = 0.33$ and $[H^+] = 0.083\ mol\,l^{-1}$

3.2.1. *Acidic attack of cobalt ferrite*

After coprecipitation, precipitate is separated and washed once with water. It is then poured into a ($2\,mol\,l^{-1}$) HNO_3 solution and stirred continuously. Titrations of Fe^{3+} and Co^{2+} as a function of time show that about 30% of the precipitate is destroyed in an hour and that degradation is complete in 48 h.

3.2.2. *Chemical stabilization of particles (Fig. 3, step 2')*

Acidic aqueous ferrofluids cannot obviously be obtained directly from manganese or cobalt ferrite. It is necessary to prevent acidic attack of particles. This is performed by an empirical process: after first step, precipitate is washed twice with water and added with a ($2\,mol\,l^{-1}$) HNO_3 solution. It is then stirred for one or two minutes and then kept at rest overnight. The bottom is separated from the supernatent, added to a boiling ($0.5\,mol\,l^{-1}$) ferric nitrate solution and kept boiling for half an hour.

This treatment prevents further particle attack and allows acidic ferrofluid synthesis. After ferric nitrate treatment, the molar ratio (cf. Equation 2) decreases from 0.33 to 0.25. So, two categories of stable ferrofluids may be obtained:

(i) anionic sols ($X = 0.33$) directly from the coprecipitate

(ii) anionic or cationic sols ($X = 0.25$) after $Fe(NO_3)_3$ treatment.

The mechanism of stabilization has not yet been elucidated. Nevertheless, the following observations may be underlined.

3.2.2.1. Ferrofluids prepared from the same initial coprecipitate exhibit different saturation magnetization [13, 18] depending on whether or not they have been treated by ferric nitrate. Size determinations performed on magnetization curves [17] allow the particle to be considered as a bulk-like magnetic core surrounded by a non-magnetic shell. For samples treated with ferric nitrate the shell thickness is systematically larger (of about 0.4 nm) than for non-treated samples [18]. This is probably due to an additional superficial alteration of particles during the $Fe(NO_3)_3$ treatment.

3.2.2.2. After ferric nitrate treatment, a noticeable size variation of particles is not observed by X-ray or by electron microscopy determinations. As a matter of fact, this size variation is probably less than experimental accuracy as shown by a rough calculation based on the following assumptions: the particle may be schematically described as a "magnetic core" of spinel structure and of MFe_2O_4 composition surrounded by a non-magnetic shell; X decreases from 0.33 to 0.25 which points to this shell containing one iron atom per MFe_2O_4. The shell thickness e for a particle of diameter D may be simply estimated assuming that specific gravity is the same in the whole

TABLE IV Surface charge density as a function of nature and molar ratio of particles

Acid or base	Nature of particles	Size		S 10^{-6} ($cm^2\,g^{-1}$)	X	α	Σ_s ($\mu C\,cm^{-2}$)	Reference
		D_{ME} (nm)	σ					
HCl	γ-Fe_2O_3	9.0	0.3	1.05		0.028	30	[20]
HNO_3	γ-Fe_2O_3	9.0	0.3	1.05		0.018	20	[20]
$HClO_4$	γ-Fe_2O_3	9.0	0.3	1.05		0.018	18	[20]
	$MnFe_2O_4$	9.7	0.23	1.06	0.25	0.025	30	[13]
					0.33	0.055	65	[13]
	$CoFe_2O_4$	11.2	0.27	0.83	0.25	0.012	18	[13]
					0.33	0.032	45	[13]
H_2SO_4	γ-Fe_2O_3	9.0	0.3	1.05		0.027	30	[20]
	$CoFe_2O_4$	11.2	0.27	0.83	0.33	0.066	95	[13]
NaOH	γ-Fe_2O_3	9.0	0.3	1.05		0.039	45	[20]
TMAOH	γ-Fe_2O_3	9.0	0.3	1.05		0.018	20	[20]
	$MnFe_2O_4$	9.7	0.23	1.06	0.33	0.033	40	[13]
	$CoFe_2O_4$	11.2	0.27	0.83	0.33	0.011	16	[13]

particle, that is

$$\frac{\text{shell mass } (FeO_{1.5})}{\text{core mass } (MFe_2O_4)} = \frac{\text{shell volume}}{\text{core volume}}$$
$$= \frac{\frac{4}{3}\pi\,[D^3 - (D - 2e)^3]}{\frac{4}{3}\pi\,(D - 2e)^3} = \frac{1}{(1 - 2e/D)^3} - 1 \qquad (3)$$

For cobalt ferrite particles (mass = 234), $e/D = 0.05$. The shell thickness corresponding to a mean diameter of 10 nm is then 0.5 nm. This value is in good agreement with the results of magnetic measurements.

3.2.2.3. The difference in behaviour between treated and non-treated particles is also illustrated by the conductimetric determinations performed on neutral particles in order to study acid or base fixation [13, 19, 20]. By conductimetric measurements on particles placed at PZC (see below), it is possible to estimate the maximum number of sites $[S_T]$ on which acids or bases can be adsorbed. The α ratio $[S_T]/[M_T]$ where $[M_T]$ expresses the total metallic concentration is an estimation of surface coverage by acids or bases. Experimental values of α for γ-Fe_2O_3 particles and for ferrite particles are shown in Table IV. Calculation of the surface charge density Σs is performed with experimental values of α [13, 20],

$$\Sigma s = \frac{\alpha}{m} N \frac{1}{S} q \qquad (4)$$

where m is the molar mass per metal atom, N Avogadro's number, q the protonic charge $= 1.6 \times 10^{-19}$ C and S the specific area of sample determined as in [13].

Σs clearly depends on the X ratio for ferrite particles. For TMAOH and for acids providing stable ferrofluids solutions (HNO_3, $HClO_4$), the mean value of Σs is about $20\,\mu C\,cm^{-2}$. Greater values observed with particles of $X = 0.33$ and in HCl or H_2SO_4 probably correspond to acidic attack of particles. Corresponding acids are known to cause degradation of particles.

Ferric nitrate treatment decreases acid fixation on the surface which seems more passive. Stable ferrofluids correspond to less reactive surfaces.

3.3. PZC step (Fig. 3, step 3)

After surface cleaning of step 2, flocculate may be directly peptized in a TMAOH solution. It may also be peptized after ferric nitrate treatment (step 2′) either in a basic (TMAOH) or in an acidic (HNO_3 or $HClO_4$) solution. To get rid of any superficial charge, it is necessary to set the flocculates at point of zero charge (PZC). For manganese and cobalt ferrites, PZC is neighbouring pH 8.0. At PZC, flocculate is washed until conductivity of supernatent reaches degassed distillated water one.

3.4. Preparation of basic and acidic sols (Fig. 3, step 4)

3.4.1. Procedure

Anionic ferrofluids are prepared by adding TMAOH solutions either directly to flocculates of step 2 or to PZC flocculates of step 3. Cationic ferrofluids are prepared by adding HNO_3 or $HClO_4$ solutions either to flocculates issued of step 2′ or to PZC flocculates obtained after step 2′.

Sols can be flocculated again by alcohol or acetone, washed with acetone and dried as a powder. Obtention of sols may be carried out again by addition of water. Basic sols have to be kept under inert (free of CO_2) atmosphere.

3.4.2. Range of sol stability

3.4.2.1. Preparation of stable sols is successfully performed with manganese and cobalt ferrite particles of size range varying from 5 to 15 nm. According to the coprecipitating base, two typical classes are obtained here for each kind of ferrite: one with $D_{RX} \sim 7$ nm, the other with $D_{RX} \sim 11$ nm for manganese ferrite; one with $D_{RX} \sim 8$ nm, the other with $D_{RX} \sim 14$ nm for cobalt ferrite.

3.4.2.2. Metallic molar concentration in sols for the two concerned ferrites, can reach $17\,mol\,l^{-1}$ which is quite larger than for any previously studied ionic ferrofluid. This molar concentration represents a volumic fraction of 0.26.

3.4.2.3. Range of total acidity (or respectively basicity) of sols is also a relevant parameter of stability. If results are expressed by a Q ratio of total acidity (or basicity) to metal atom concentration

$$Q = \frac{[H^+] \text{ (or } [HO^-])}{[Fe(III) + M(II)]} \qquad (5)$$

typical Q values vary from 0.04 to 0.06 for acidic ferrofluids in HNO_3 as well as for alkaline ferrofluids in $[N(CH_3)_4]OH$.

3.4.3. Applications

Easily available amounts of very concentrated ferrofluids have already allowed new experiments on the wetting of a platinum wire to be carried out [21]. These experiments not previously performed are of interest for magnetic studies of wetting.

It has been shown [18] that a large anisotropy constant of cobalt ferrite enables microscopic needle synthesis of this magnetic compound. It is hoped that new applications in the engineering field may arise as a result of this behaviour.

4. Conclusion

Preparation of ferrofluids based on manganese and cobalt ferrites may be performed by adaptation of Massart's procedure on maghemite.

Particle size and polydispersity depend on the synthesis parameters and can be controlled, namely by the nature of coprecipitating base, the pouring order of reagents and the mixing speed.

A chemical stabilization of particles allows these new ionic ferrofluids to be prepared in acidic as well as in alkaline mediums. Their concentration can reach $17\,mol\,l^{-1}$ which corresponds to 0.26 volumic fraction.

The remarkable properties of these two new magnetic liquids have already allowed new experiments in magnetism topics, and there are very promising practical and theoretical applications.

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