Preparation of Dy-ferrite Ferrofluids and Magnetochemical Studies on the Superparamagnetism

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This paper reports unprecedented preparation of Dy-ferrite water-based ferrofluids stabilized by polymeric surfactant PMAA. The stability of ferrofluids was characterized in terms of the equation of criterion for the stability of ferrofluids. Magnetic susceptibility was measured with a Faraday-type magnetic balance at different temperature and with different magnetic field intensity. According to the Langevin function, superparamagnetism of Dy-ferrite ferrofluids has been confirmed by the curves of saturation magnetization σ versus H/T, and the blocking temperature is between 160 and 200 K. In terms of the simplified Langevin function in the low magnetic field, the average particle size is 20 nm that coincides with the result evaluated by FHMW. In addition, chemical analysis, infrared spectra and Mössbauer spectroscopy were utilized to analyze the main components of the ferrofluids.

Keywords   PMAA, Dy-ferrite ferrofluids, stability, superparamagnetism

Introduction

Magnetic fluids are stable colloidal suspensions of ultrafine magnetic particles dispersed in a carrier liquid.[1] They not only exhibit strong magnetism like their bulk counterparts, but also have fluidization qualities. In the presence of external magnetic field, ferrofluids exhibit unique properties. The surface density of ferrofluids can be changed with the applied magnetic field strength. Furthermore, ferrofluids can orient accurately under application of a magnetic field. Based on their high saturation magnetization and superparamagnetic properties, magnetic fluids have wide applications in chemical engineering, environmental protection, medicine and mechanics.

In several studies, many reports have focused on the synthesis of stable oil-based magnetic fluids. While applications of oil-based ferrofluids are relatively limited, the preparation of water-based magnetic fluids has attracted a great deal of attention. In this paper, we report the preparation of aqueous Dy-ferrite magnetic fluids stabilized by polymeric surfactant PMAA. Superparamagnetism of the ferrofluids is also investigated.

Experimental

Methacrylic acid in which polymerization inhibitor had been eliminated was of commercial grade. Polymethyl acrylic acid (PMAA) was prepared from methacrylic acid and initiator potassium persulphate.

A mixed solution of ferrous, ferric and dysprosium(III) ions in the molar ratio 1:4:1 was prepared by dissolving 0.6 mol/L $FeSO_4$, 1.2 mol/L $FeCl_3$, and 0.6 mol/L $Dy(NO_3)_3$ with vigorous stirring. As the solution was heated to 50°C, $NH_3 \cdot H_2O$ solution was added until pH reached 10. The mixture was subsequently maintained at 60°C for 30 min.[2] PMAA was added with constant stirring to the solution at concentration up to 0.655 g/100 mL. The crystal growth was allowed to proceed for 30 min at 80°C while pH = 7. The precipitates were isolated from the solvent by magnetic sedimentation. The water-washing procedure was repeated several times until no SO_4^{2-} or Cl^- was detected with

$BaCl_2$ or $AgNO_3$ solution.

The nanoparticles and some water were combined at 50℃ and stirred for 30 min at 1×10^3 r/min. The preparation of the sample was performed by redispersing in an ultrasonic bath for 20 min, centrifuging the solution for a further 5 min, filtering the precipitates, and thus obtaining a stable water-based ferrofluid.[3]

Results and discussion

Long-term stability

One of the most important properties is long-term stability of ferrofluids that often display aggregation and precipitation on standing. It has been demonstrated that the temperature, pH of suspensions, and surfactant concentration play a vital role in stabilizing the ferrofluids. PMAA adheres to the surface of magnetic nanoparticles, creating a net repulsion between the particles and stabilizing the colloidal suspensions of magnetite. However, using more surfactant does not lead to more stable ferrofluids. The pH value of the suspensions is another one of the most important factors that influence magnetism and stability of ferrofluids. On addition of dilute ammonia, only a small portion of Dy^{3+} can co-precipitate with Fe^{2+} and Fe^{3+}, and consequently the rest of Dy^{3+} was removed by washing. Especially, the pH value influenced the ferrofluids greatly when PMAA was used.

Reimerst and Khalaflla have reported that the stability of ferrofluids can be described by Eq. (1).

$$I = (\rho_I - \rho_W)/(\rho - \rho_W) \qquad (1)$$

The density ρ of freshly prepared samples and the density ρ_I of samples which had been laid for 100 h were measured. The density ρ_W of solvent was also determined.[4] The indexes of stability for a number of ferrofluids obtained in this manner are presented in Figs. 1 and 2.

Fig. 1 displays that the ferrofluid is the most stable at PMAA concentration of 0.655 g/100 mL when pH of Dy-ferrite suspension is 7. PMAA has both carboxylate groups on alternate carbon atoms and hydrocarbon chains, and consequently the polymer can provide double surfactant layers within a single molecule. Hydrophilic carboxylate groups not only attach to the particles, but also interact with the carrier liquid, while hy-

drophobic hydrocarbon chains provide the steric stabilization.[5] In a certain range, the effect of this dispersion and stabilization increases with increasing PMAA concentration. However, when PMAA concentration is beyond an optimal value, the polymeric molecule may intertwine, which would lead the particles to aggregate and thus reduce the stability of ferrofluids.
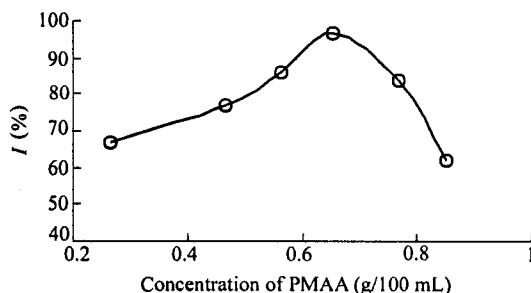

Fig. 1   Effect of PMAA concentration on the index of stability of ferrofluids prepared at pH 7.
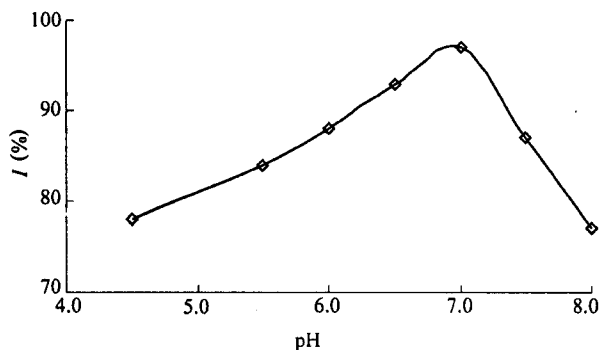

Fig. 2   Effect of pH value on the index of stability of ferrofluids prepared at PMAA concentration of 0.655 g/100 mL.

Fig. 2 shows that an optimal stability is achieved near neutral pH. Addition of PMAA, in un-ionized form, to an ammoniacal Dy-ferrite suspension gives ferro fluids. The charge-stabilized Dy-ferrite particles, first formed by preparation from basic solution, will have surface bound OH^- ions, which react with PMAA to leave the carboxlate group bound to the particle surface.[3] Meanwhile, the extremely high affinity between Dy-ferrite and the carboxylic acid group of PMAA makes not only the orientation of the surfactant at the particles/surfactant interface favorable but also the chemisorption reaction between them. Once the surfactant has been adsorbed on the Dy-ferrite particles at pH 7 (close to the isoelectric point of magnetite), the number of accessible sites for further crystal growth will be reduced, leading

to termination of crystal growth and stabilization of fer-
rofluids.[6]

Analysis of the main components

The contents of Fe and Dy were determined by
spectrophotometry, respectively (as shown in Table 1).
Sulfosalicylic acid and azochlorophosphon (III) were uti-
lized as indicators. In this manner, we find that samples
A1 and A2 have the following stoichiometry: $Dy_xFe_{3-x}O_4$
($x = 0.10$—0.20).

Table 1 Contents of Dy and Fe in the ferrofluids

Sample	Main components	Volume (mL)	Absorbance	Content (mg)
A1	Fe	2	0.283	0.0753
	Dy	2	0.123	8.15×10^{-3}
A2	Fe	2	0.252	0.0605
	Dy	2	0.186	1.08×10^{-2}

IR spectrum of the sample shows three absorption
bands at 3450 cm^{-1}, 1770 cm^{-1} and 2800—2960 cm^{-1},
the first two peaks being assigned to the COOH and C =
O stretching vibration of PMAA, respectively, and the
last to the CH_3 and CH_2 stretching vibration of PMAA.

Magneto-chemistry studies

In this study, we have synthesized several kinds of
ferrofluids by varying the dosage of Dy (III). Conse-
quently, it is observed that with increase in Dy (III)
content (Table 1), the magnetization increases (as
shown in Table 2). The experimental data of magnetic
susceptibility (χ_m) is determined by the magnetic ba-
lance at various magnetic field (H). Magnetization
(σ_m) can be calculated by the following formula:

$$\sigma_m = \chi_m \cdot H \qquad (2)$$

Table 2 Magnetization with different Dy(III) contents at various magnetic field (10^{-4} T·cm^{-3}·g^{-1})

H (mT)	45	95	170	230	280	340
A1	9.847	15.066	24.230	29.550	35.412	39.587
A2	18.151	29.023	42.431	49.600	55.351	68.569

The magnetic properties of magnetite that make it a
desirable component of ferrofluids are derived from its
crystal structure. Magnetite crystallizes in the inverse
spinel structure above 120 K. The inverse spinel struc-
ture is formed by a close-packed oxygen lattice, in which
one-eight of tetrahedral (A) and one-half of octahedral
(B) interstitial sites are occupied by iron ions. A unit
cell contains 8 iron ions on A-sites, 16 iron ions on B-
sites, and 32 oxygen anions. Electron spins of iron(III)
ions on octahedral B-sites are aligned antiparallel to
these on tetrahedral A-sites; therefore, no net magneti-
zation is observed from these ions. The iron(II) ions in
adjacent to octahedral sites, leading to a net magnetiza-
tion. This arrangement of antiparallel spins throughout
the solid that do not completely cancel is referred to as
ferrimagnetism.[7] Substitution of some trivalent ions
which have higher magnetic moment for Fe^{3+} in inverse
spinel ferrites, is made for special magnetic and electri-
cal function. The introduction of Dy^{3+} on octahedral B-
sites will enhance the saturation magnetization since the
substitution of Dy^{3+} for Fe^{3+} will have a net moment and
alter their magnetic and electric properties.[8] The data in
Table 2 shows that sample A2 has higher magnetism than
that of A1, because of the enhanced dosage of Dy^{3+}.

Highly dispersed in a carrier liquid, colloidal parti-
cles in ferrofluids are very fine. As the particles reach
the critical volume, their energy of anisotropy KV is cor-
respondingly reduced. When it is less than thermal ener-
gy kT ($KV < kT$), Brownian motion orients the particles
and the direction of magnetization is randomly arranged.
Activated by thermal energy kT, magnetization of the
particles can overcome the energy barrier of anisotropy
and exhibit properties similar to paramagnetic matters.
Such phenomenon is called superparamagnetism. On the
contrary, magnetization is fixed on easy axis of
anisotropy if $KV > kT$, which is called "blocking". Ac-
cording to the theory of superparamagnetism,[9] monodis-
persed magnetic fluids is described by the Langevin

function:

$$\frac{\sigma}{\sigma_s} = \coth\frac{\mu H}{kT} - \frac{kT}{\mu H} \qquad (3)$$

where σ/σ_s is the ratio of magnetization, μ the magnetic moment of a particle, H the applied magnetic field strength, k the Boltzmann constant, and T the absolute temperature. On the basis of Eq. (3), the curves of σ/σ_s (or σ) obtained from experimental data at various H and T versus H/T should overlap each other in a single line, which is the criterion of superparamagnetism. Saturation magnetization σ_s of magnetic particles is a definite value, so we can judge whether the samples have superparamagnetism from the curves of σ/σ_s (or σ) versus H/T.
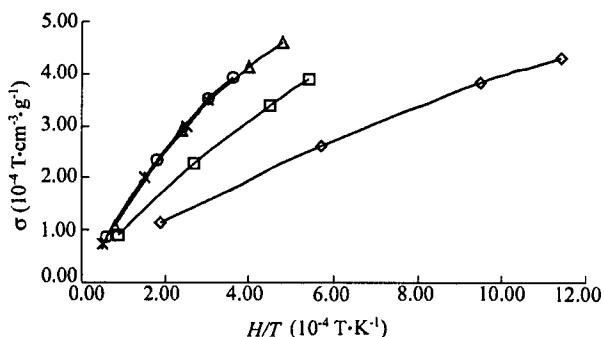
Fig. 3 Relationship between saturation magnetization σ and H/T at various temperature. $\Diamond$: 77 K; $\square$: 160 K; $\triangle$: 200 K; $\bigcirc$: 248 K; $*$: 275 K.

Fig. 3 displays curves of saturation magnetization σ versus H/T at various temperature. In terms of the criterion of superparamagnetism, these magnetic particles exhibit superparamagnetism at 200 K and above. The blocking temperature of the particles is shown to be in the range from 160 to 200 K. As far as a single-disperse system is concerned, the average particle size can be calculated in terms of the simplified Langevin function in the low magnetic field from σ determined at different temperature.

When $\mu H/kT \ll 1$, Langevin function can be simplified as

$$\sigma = \frac{\sigma_s \mu H}{3kT} \qquad (4)$$

in which $\mu = v\sigma_s\rho$, where v is the volume of magnetic particle, ρ the density of the sample, σ_s is saturation magnetization. The relationship between v and the initial slope of the curve of σ versus H/T is characterized by

$$v = \frac{3k}{\sigma_s^2\rho}\text{slope} \qquad (5)$$

Applying these formulas to our system, the average particle size of 20 nm is obtained. This mean particle size agrees with the result obtained by XRD (FWHM), and the direct observation from transmission electron microscopy (TEM). Fig. 4 displays the Dy-ferrite nanoparticles with fairly uniform size.
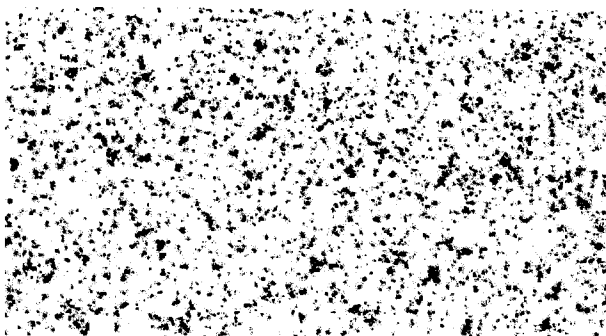
Fig. 4 TEM micrograph of surfactant-coated magnetic particles (×40000).

Mössbauer spectra

Sample 3 and 4 were ferrite magnetic fluid and Dy-ferrite magnetic fluid, respectively. The Mössbauer spectra of them at RT were fit by three groups of sextets (as shown in Table 3).

Compared with data in the references, sextet 1 and 2 of both samples can be attributed to Fe ions on A and B sites, respectively. Fe_3O_4 on the surface could be a contribution to sextet 3 which has the minimum hyperfine field H. By comparison of parameters of both samples, there are noticeable differences in both the spectral area and hyperfine field. The two groups of parameters are in close relation to the relative content of Fe ions on A and B sites. Other preparative conditions being equal, these variances are probably caused by the addition of Dy ions.

Table 3 Fitting data of three groups of sextets of Mössbauer spectra[a]

Sample	Fitting spectra	IS (mm/s)	QS (mm/s)	H (kOe)	A
	sextet 1	0.38 + 0.02	0.01 + 0.01	482.79 + 0.54	0.470 + 0.022
3	sextet 2	0.47 + 0.05	0.05 + 0.04	442.68 + 2.18	0.336 + 0.041
	sextet 3	0.50 + 0.24	− 0.01 + 0.10	380.03 + 8.17	0.206 + 0.036
	sextet 1	0.38 + 0.02	0.01 + 0.01	477.74 + 0.49	0.308 + 0.018 ⁻
4	sextet 2	0.41 + 0.04	0.00 + 0.02	440.35 + 1.58	0.422 + 0.033
	sextet 3	0.49 + 0.16	0.00 + 0.07	375.24 + 8.03	0.261 + 0.036

[a] IS: isomer shift; QS: quadrupole shift; H: magnetic hyperfine field; A: relative absorption area.

Conclusions

We have shown an effective way to synthesize sta-ble, water-based Dy-ferrite magnetic fluids stabilized by polymeric surfactant PMAA. To obtain such ferrofluids, proper surfactant concentration, temperature, and pH value are required. According to the Langevin function, the curves of saturation magnetization σ versus H/T are obtained and superparamagnetism of the ferrofluid has been confirmed. Its blocking temperature is between 160 K and 200 K. In terms of the simplified Langevin function in the low magnetic field, the average particle size is 20 nm that is identical with the results evaluated by FHMW and TEM. The synthetic route is reliable and holds promise for further progress in synthesizing stable water-based magnetic fluids consisting of rare-earth metals.

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