



Aqueous-based magnetite magnetic fluids stabilized by surface small micelles of oleolysarcosine

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Abstract

The adsorption of *N*-oleylsarcosine onto in water dispersed magnetite nanoparticles were investigated at different concentrations and pH values. The coated nanoparticles surface became hydrophobic at a molar ratio of *N*-oleylsarcosine:Fe₃O₄ below 0.22:1 within a pH range of 5–9.5. Aqueous-based magnetic fluids could not be obtained. A hydrophilic surface was observed at a molar ratio of *N*-oleylsarcosine:Fe₃O₄ above 0.37:1 and at pH levels ranging from 6 to 8.5. Stable aqueous-based magnetic fluids could be prepared. The magnetite particles flocculate at pH levels below 5.5 or above 8.5. The hydrophobic behavior was explained assuming a monolayer adsorption mode. On the other hand, the hydrophilic properties were caused by a bilayer adsorption structure. This hypothesis was in overestimation with results of infrared (IR) spectroscopy and photon correlation spectroscopy of the prepared magnetic fluids. The influences of pH levels on the formation of *N*-oleylsarcosine micelles were also discussed to explain the pH-dependant formation of bilayer adsorption structure, i.e. surface small micelle structure. It was indicated that it became difficult for *N*-oleylsarcosine adsorb at the water–air interface, or adsorb at the nanoparticles surfaces in the form of surface small micelles at pH levels above 8.5. Besides, the aqueous-based magnetic fluids were also characterized by magnetization curve determinations.

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1. Introduction

Aqueous-based magnetite magnetic fluids (MMFs in brief) are attracting extensive attentions for their applications in biological and medical diagnosis and therapy [1–3]. One approach for the preparation of

aqueous-based MMFs is to coat the magnetite nanoparticles with surfactant bilayers [4]. In this case, carboxylic acids were often used. The adsorption of surfactant molecules of carboxylic acids at magnetite particles–water interfaces includes two steps [5,6]: firstly, the surfactant molecules chemisorb at metal oxide particle surfaces through their carboxylic acid head groups, and their non-polar tails extend into carrier liquids, which results in hydrophobic magnetite nanoparticles. After the first step of adsorption

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achieves to equilibrium and the concentration of the surfactant monomer attains to its critical surface small micelle concentration (HMC) value (at the point of 24–86% critical micelle concentration value), the second step of adsorption begins. Under a suitable condition, a typical bilayer adsorption structure in the form of surface small micelles will be established through hydrophobic associations between the non-polar tails of primary and secondary surfactant molecules, which gives rise to aqueous-based magnetic fluids. Shen et al. [7] and Fu et al. [8] have demonstrated and investigated the bilayer coating of fatty acids at the magnetite nanoparticles surfaces. However, the effect of pH levels on the formation of bilayer adsorption structure has not been discussed yet.

In this study, the adsorption of *N*-oleoylsarcosine (NOSARK in brief) at magnetite nanoparticle surfaces in the aqueous solutions was investigated at different surfactant concentrations and pH values. Magnetite nanoparticles coated with NOSARK were characterized by infrared (IR) spectroscopy and photon correlation spectroscopy analysis. Since the formation of surface small micelles is correlative with the formation of micelles in the solutions. The influences of pH levels on the formation of NOSARK micelles in aqueous solutions were also discussed. For this purpose, the solubility and CMC values of NOSARK at different pH levels were determined. Furthermore, the resonance scattering spectra and photon correlation spectra of NOSARK solutions at different concentration and different pH levels were recorded. Besides, the aqueous-based MMFs were characterized by magnetization curve determinations.

It was found that the typical bilayer adsorption mode formed at a molar ratio of *N*-oleoylsarcosine: Fe_3O_4 above 0.37:1 and at pH levels ranging from 6 to 8.5. Coincide with it, the aqueous-based MMFs were stable just in the pH ranges of 5.5–8.5. Since NOSARK is biocompatible [9], this performance is prospected to be applied in the pH dependence drug deliveries and releases.

2. Materials and methods

Magnetite (Fe_3O_4) nanoparticles were synthesized by means of co-precipitation method [10], by alkalizing an aqueous mixture of ferrous sulfates (FeSO_4)

and ferric chlorides (FeCl_3). After the magnetite particles were washed by distilled water, NOSARK were added, and then pH values of the solutions were adjusted by adding acetic acids (HAC), or 1 mol/l hydrochloric acid (HCl), or 25 wt.% ammonia ($\text{NH}_3\cdot\text{H}_2\text{O}$). The mixing solutions were heated at 60 °C with stirring. The concentration of Fe_3O_4 was about 55 g/l.

By using Bio-Rad FTS3000 FT-IR spectrometer, infrared spectra were recorded. The magnetite particles coated with or without NOSARK were mixed with KBr powder and pressed to pellets as samples.

To determine the range of pH levels for the stability of the MMFs, the flocculation of the aqueous-based MMFs was observed after the pH levels of MMFs were adjusted by the addition of 0.5 mol/l HCl solution or 1 mol/l sodium hydroxide (NaOH) solution.

To obtain CMC value of NOSARK, the surface tensions of NOSARK solutions at different concentrations and at pH 6.7 or 10 were measured. The surface tensions of solutions were measured by plate method on the Krüss K12 Surface Tensiometer.

The photon correlation spectra of NOSARK solutions or diluted MMFs were recorded on Brookhaven Instrument Corporation B I-200SM Goniometer. He/Ne laser with a wavelength of 633 nm was used. Detector angle was 90.0°. First delay was 1.0 μm , last delay was 100 ms and elapsed time was 2 min. 30, 400, 800, and 1600 mg NOSARK was diluted to 100 ml by using Britton–Robinson buffer solutions at different pH levels to obtain NOSARK solutions at different concentrations. Octane-based MMFs in the density of 1.2 g/ml was diluted to 4800 times and 9600 times, and water-based MMFs in the density of 1.1 g/ml were diluted to 2400 times.

The resonance scattering spectra of NOSARK solutions were recorded on the Spectronic Amminco Bowman Series 2 Luminescence Spectrometer. The excitation and emission monochromator were coupled and adjusted to scan simultaneously through the range from 200 to 800 nm. The slit was 10 nm in width, and the negative voltage of photomultiplier was 400 V. Twenty micrograms NOSARK was diluted to 100 ml by using Britton–Robinson buffer solutions at different pH levels to obtain NOSARK solutions with the concentration of 200 mg/l.

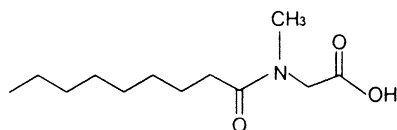
The magnetization curve of MMFs was measured by a Vibration Sample Magnetometer.

3. Results and discussion

3.1. IR spectroscopy analysis and the adsorption characteristics of NOSARK at magnetite nanoparticle surfaces

The schematic structural of NOSARK is shown as Scheme 1. The characteristic frequencies of NOSARK are shown in Table 1 [11]. The 1737 cm^{-1} band attributed to stretching vibration mode of $-\text{COOH}$ groups. The spectra of magnetite nanoparticles and those coated with NOSARK are shown in Fig. 1. The 582 cm^{-1} band belongs to the stretching vibration mode of $\text{Fe}-\text{O}$ bonds in Fe_3O_4 [12].

When the NOSARK: Fe_3O_4 molar ratio was below 0.22:1, the coated nanoparticles were hydrophobic which suggested that the non-polar tails of NOSARK extended to water. Shown as curve 2 in Fig. 1, the 1739 and 950 cm^{-1} bands of COOH groups in NOSARK disappeared, but the 1616 and 1396 cm^{-1} bands of COOM (M represents metal ions) groups appeared, which indicated that the COOH groups of NOSARK reacted with the surface OH groups of Fe_3O_4 particles resulting in the formation of the iron carboxylate. So the adsorption mode can be presented as Fig. 2a, that is



Scheme 1.

Table 1
The characteristic frequencies of *N*-oleoylsarcosine

Bands (cm^{-1})	Remarks
2922	$\nu_{\text{as}}^*(\text{C}-\text{H})$ for $-\text{CH}_2$
2856	$\nu_{\text{s}}^*(\text{C}-\text{H})$ for $-\text{CH}_2$
1737	$\nu_{\text{s}}(\text{C}=\text{O})$ for carboxylic acid $-\text{COOH}$ dimer
1640	$\nu_{\text{s}}(\text{C}=\text{O})$ for acylamino $-\text{CON}-$
1465	$\delta^*(\text{C}-\text{H})$ for $-\text{CH}_2-$
1406	$\nu_{\text{s}}(\text{C}-\text{N})$ for $-\text{CON}-$ or $\nu_{\text{s}}(\text{C}-\text{O})$ for $-\text{COOH}$
1283	$\nu_{\text{s}}(\text{N}-\text{C})$ for $-\text{CON}-\text{C}-$
1205	The couple between $\nu_{\text{s}}(\text{C}-\text{O})$ and $\delta(\text{O}-\text{H})$ for $-\text{COOH}$
950	$\delta(\text{OH}\cdots\text{O})$ for $-\text{COOH}$ dimer

ν_{as}^* : asymmetrical stretching vibration; ν_{s}^* : symmetrical stretching vibration; δ^* : deformation vibration.

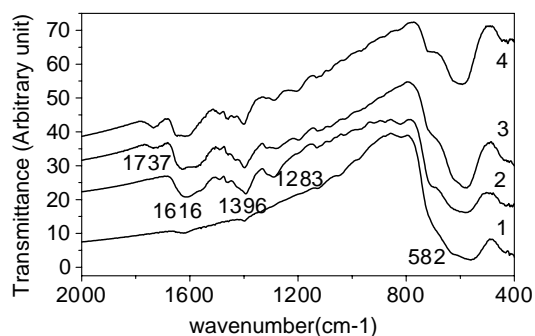


Fig. 1. FT-IR spectra of magnetite nanoparticles: (1) non-coated; (2) with the NOSARK: Fe_3O_4 molar ratio below 0.22:1; (3) with the NOSARK: Fe_3O_4 molar ratio above 0.22:1 but below 0.37:1; and (4) with the NOSARK: Fe_3O_4 molar ratio above 0.37:1.

to say, monolayer NOSARK molecules chemisorbed at the nanoparticles surfaces.

The chemisorption quantities can be estimated from the intensity ratio of 1616 or 1396 cm^{-1} band to 582 cm^{-1} band. According to this, it was found that the quantity of chemical adsorption increases with the addition of NOSARK, when the NOSARK: Fe_3O_4 molar ratio was below 0.22. However, the influence of the pH levels on this chemisorption was not critical at least within a pH range of 5–9.5.

When the NOSARK: Fe_3O_4 molar ratio was increased above 0.22:1 but below 0.37:1, the nanoparticles were still hydrophobic, and at low pH levels, the nanoparticles congregated to large particles as the result of hydrogen bond between the COOH groups. Their IR transmission spectra (shown as curve 3) showed that the 1730 cm^{-1} band appeared, which indicated that some additional NOSARK molecules adsorbed at the primary molecules surface with free COOH groups. The adsorption mode can be presented as Fig. 2b (for low pH levels) or Fig. 2c (for high pH levels). The typical bilayer adsorption structure has not formed at any pH levels due to the lack of NOSARK molecules.

When the NOSARK: Fe_3O_4 molar ratio was increased up to 0.37:1, the typical bilayer adsorption structure formed, but just within a pH range of 6.0–8.5, i.e. the surface small micelles just formed in the pH range of 6.0–8.5. Their IR transmission spectra were shown as curve 4 in Fig. 1. The 1730 cm^{-1} band was strengthened, which indicated the increase of the physisorption molecules, corresponding to the

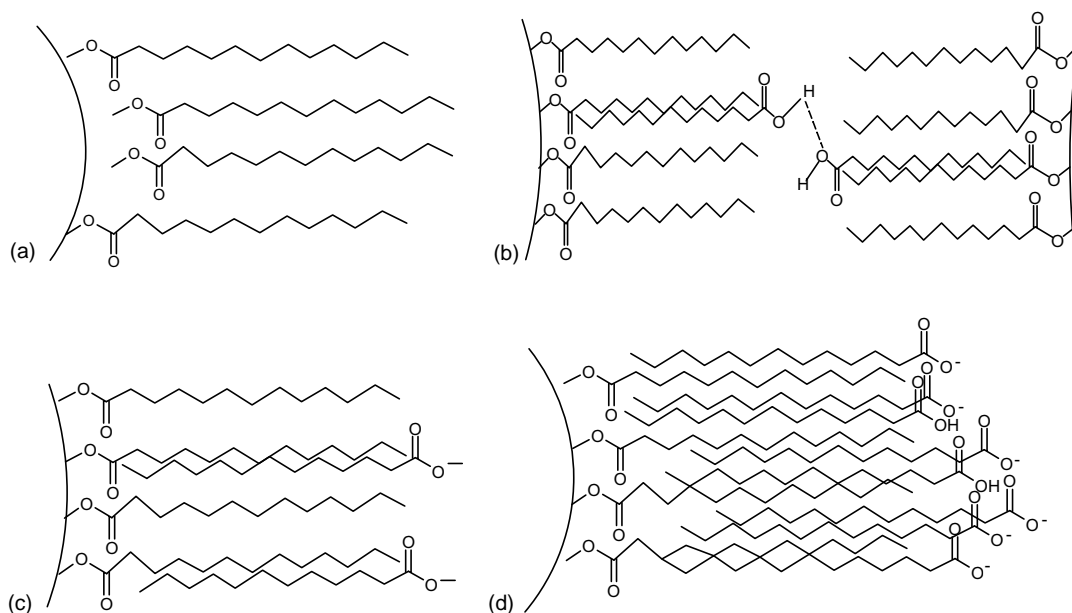


Fig. 2. Four typical adsorption modes: (a) single layer; (b) part bilayer; (c) part bilayer (secondary was anions); and (d) typical bilayer.

formation of bilayer adsorption structure. The adsorption mode can be presented as Fig 2d. The preliminary electrophoresis experiments showed that the nanoparticle surfaces were negatively charged. This fact indicated that the secondary molecules were in the form of anions, which prevented the nanoparticles from aggregation through steric repulsion and electrostatic repulsion.

Besides, it was found that the magnetic liquids were stable in a pH range of 5.5–8.5. This means that when the pH levels of MMFs are out of the range of 5.5–8.5, disassembly of surface small micelles at the nanoparticle surface occurs.

3.2. The influence of pH levels on the solubility of NOSARK and the formation of NOSARK micelles in aqueous solutions

NOSARK had low solubility in water (less than 60 mg/l) and its saturation solution was at pH 5.3. Its solubility increased with the pH levels of the solutions when ammonia was added. When equivalent ammonia was added, the solution in the concentration of 30 g/l became half-transparent and the pH level achieved to 6.7. (The ionization constant of 6.8×10^{-5} was estimated from this.) When the pH levels of the

solutions were adjusted to 7.5, the solubility of NOSARK improved greatly and the solutions in the concentration of 30 g/l became transparent. According to its ionization constant, it was known that most of NOSARK molecules existed in the form of anions in aqueous solutions above pH 6 and the anions fractions increased with the pH levels.

The surface tensions of the solutions at pH 6.7 and 10 with different concentration of NOSARK are shown in Table 2. It can be seen that the CMC values of NOSARK in the aqueous solutions at pH 6.7 and pH 10 were about 60 and 125 mg/l, respectively. That is to say, at pH 6.7, when the concentration of solution achieves to 60 mg/l, micelles begin to form, while at pH 10, the concentration of solution should achieve to 125 mg/l. At this concentration, the adsorption of surfactant at water–air interface attains equilibrium and the concentration of micelles increase with the surfactant added. Table 2 also shows that the surface tensions of the solutions at pH 6.7 declined more than at pH 10 which suggested that more molecules adsorbed at water–air interface at pH 6.7 than at pH 10.

The results of photon correlation spectra of NOSARK solutions at different concentrations and pH levels are shown as Table 3. The photon count rate increased with the concentration of NOSARK.

Table 2

Surface tensions of *N*-oleoylsarcosine solutions at different concentrations and pH levels

pH (mN/m)	Concentration (mg/l)									
	25	50	60	75	85	100	110	125	135	150
6.7	30.0	28.5	27.8	27.8	27.6	27.8	27.7	27.6	27.7	27.6
10	40.1	39.9	36.0	36.2	35.2	35.1	34.8	34.3	34.1	34.3

Table 3

The results of photon correlation spectra of *N*-oleoylsarcosine solutions at different concentrations and pH levels

pH	Photon count rate (cps)				Mean diameter (nm)			
	300 mg/l	4 g/l	8 g/l	16 g/l	300 mg/l	4 g/l	8 g/l	16 g/l
5.4	22.1k	112k	118k	88k	95	92	116	96.9
6.5	–	1.4k	1.7k	5.5k	–	2.0	15.2	25.5
7.5	493	920	1.4k	4.5k	–	4.7	2.0	18.8
8.5	20	1.1k	2.1k	4.1k	–	7.3	4.3	29.6
9.5	–	1.5k	3.0k	6.3k	–	18.8	34.9	64.2

It decreased with the pH values when pH below 7.5, increased with pH values when pH above 7.5 and achieved to a minimum at pH levels around 7.5. The mean hydrodynamic diameters of NOSARK micelles were not remarkably affected by the concentration of NOSARK at low concentrations, but they increased obviously at the concentration of 16 g/l. It also achieved to a minimum at pH around 7.5 and increased greatly at pH 9.5. The diameters of particles were about 90–120 nm at pH 5.5, which suggested that NOSARK molecules were insoluble and congregated together.

Coincide with it, the resonance scattering spectra of NOSARK solutions (shown as Fig. 3) in the concentration of 200 mg/l at different pH levels indicated that the scattering intensity achieved to a minimum at pH around 7.5.

From above, it was known that when the pH levels was low, for example below 6, the solubility of NOSARK was very low and NOSARK molecules tended to congregate together and cannot array orderly at the primary molecules surface through hydrophobic associations. On the other hand, when the pH levels were above 8.5, the solubility of NOSARK in water increased obviously and NOSARK molecules tended to disperse in water in the form of micelles, which resulted in the increase of photon count rate and micelle diameters in photon correlation spectra. It became difficult for them to adsorb at the water–air

interface, or adsorb at the primary molecular surfaces through hydrophobic association. So the surface small micelles just formed within a pH range of 6.0–8.5.

3.3. The characterization of aqueous-based MMFs

Table 4 shows the results of photon correlation spectra of MMFs stabilized by NOSARK. It was indicated that the mean hydrodynamic diameter of monolayer coated nanoparticles was about 10 nm, and the bilayer coated nanoparticles was about 20 nm, which demonstrated the adsorption mode suggested

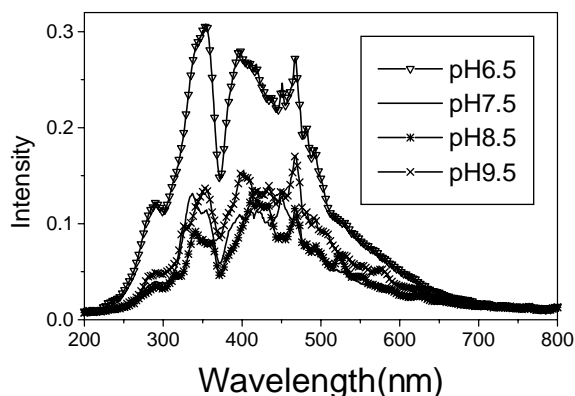


Fig. 3. The resonance scattering spectra of *N*-oleoylsarcosine solutions at different pH levels.

Table 4
The results of photon correlation spectra of diluted magnetic fluids

Samples	Mean diameter (nm)
Octane-based MMFs diluted to 4800 times	8.1
Octane-based MMFs diluted to 9600 times	11.9
Aqueous-based MMFs diluted to 2400 times	20.7
Aqueous-based MMFs standing for 1 day after diluted	40.6

above. However, the hydrodynamic diameters increased when the diluted water-based MFFs were standing for 1 day, which suggested that the MFFs became unstable after a serious dilution.

The magnetization curve of an aqueous-based MMFs is depicted as Fig. 4, the volume fraction of magnetite was about 4.5%. It exhibited a good superparamagnetic property with zero coercivity and remanence and its saturation magnetization was 28.7 mT. The magnetite core diameter of 11.5 nm was calculated from the initial section using the formula [13].

$$d_m = \left(\frac{18\chi kT}{\pi\mu_0 M_s M_I} \right)^{1/3}$$

where d_m is the particle diameter determined by the initial section of the fluid magnetization curve, χ is the magnetic susceptibility of a MMFs, k is the Boltzmann constant, T is the absolute temperature, μ_0 is the vacuum magnetic permeability, M_s is the saturation magnetization of MMFs, and M_I is the saturation magnetization of particles material. This value is higher than the result obtained from X-ray refraction analysis of modified nanoparticles [10].

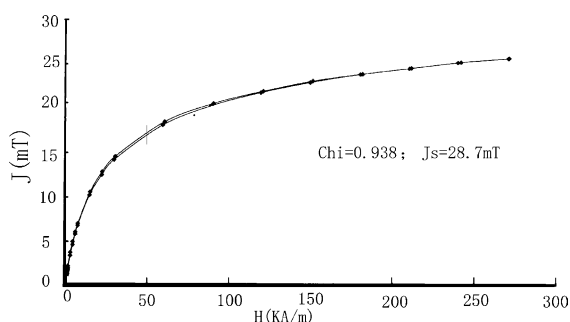


Fig. 4. The magnetization curve of aqueous-based magnetic fluids in the density of 1.19 g/cm³.

4. Conclusion

At a molar ratio of NOSARK:Fe₃O₄ below 0.22:1, only a monolayer of NOSARK adsorbed at nanoparticle surfaces. At a molar ratio of NOSARK:Fe₃O₄ above 0.37:1 and at pH levels ranging from 6 to 8.5, the typical bilayer adsorption mode formed. Coincidence with it, the aqueous-based MMFs were stable just in the pH ranges of 5.5–8.5. This was because when the pH levels was below 6, the solubility of NOSARK was very low, NOSARK molecules tended to congregate together and cannot array orderly around the primary molecules through hydrophobic associations. On the other hand, when the pH levels were above 8.5, the solubility of NOSARK in water increased obviously and NOSARK molecules tended to disperse in water in the form of micelles. It became difficult for NOSARK molecules adsorb at the water–air interface, or adsorb at the nanoparticles surfaces in the form of surface small micelles.

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