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RESEARCH ARTICLE

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Preparation of Fe_3O_4 magnetic fluid by one-step method with a microemulsion reactor

Abstract A W/O microemulsion was prepared with Span80-PS (petroleum sulfonate) as complex emulsifier, isopropanol as cosurfactant and kerosene as oil phase. The optimal constituents of microemulsion were found from pseudoternary phase diagrams: the mass ratio of Span80 to PS was 4:1 and complex surfactant to cosurfactant was 1:1. The Fe_3O_4 magnetic fluid was obtained by one-step method with the W/O microemulsion as microreactor to synthesize magnetic nanoparticles (reaction temperature was 30℃ and reaction time was 5 h) and kerosene as carrier liquid. The magnetic fluid was investigated by TEM, XRD and fluorescence microscope. The magnetism was determined by Gouy magnetic balance. The average particle size of Fe_3O_4 was 7.4 nm, and magnetic particles were well-dispersed. The stable Fe_3O_4 magnetic fluid with good magnetism may be produced by one-step method in the W/O microemulsion. Accordingly, the traditional preparation method of magnetic fluid can be simplified greatly.

Keywords microemulsion, magnetic fluid, one-step, pseudoternary phase diagram

1 Introduction

Magnetic fluid, also called ferrofluid, is a dynamically stable colloid dispersion containing surfactant-coated magnetic particles (average diameter < 10 nm) which dispersed evenly in a carrier liquid [1]. Magnetic fluid had been widely applied in sealing fields such as vacuum sealing, toxic gas sealing, dust-proof sealing, and many difficulties in sealing engineering were overcome [2]. Furthermore, magnetic fluids have showed prospective applications in drug-delivery, biology and environment protection [3–6]. However, the reported magnetic fluid preparation methods usually included two steps: synthesis of magnetic particles and dispersal into a carrier liquid under mechanical force [7–9]. In such technical processes, the pre-synthesized particles are easy to aggregate in the second processing, which would affect the stability and the magnetism of the ferrofluid.

In this paper, a new method preparing Fe_3O_4 magnetic fluid was introduced. The optimized W/O microemulsion system was taken as a microreactor to synthesize almost monodispersed particles, and dispersed simultaneously into the oil phase of microemulsion. The Fe_3O_4 magnetic fluid was obtained with the synthesis of the magnetic nanoparticles in this so-called 'one-step method'. The experimental results showed the average diameter of the synthesized particles was under 10 nm with narrow size distribution, and the magnetic fluid was stable with good magnetic properties. With one-step method, the traditional preparation process of ferrofluid can be simplified greatly in guaranteeing of Fe_3O_4.

2 Materials and methods

2.1 Materials

All reagents were available in Chinese market and used without further purification, and the used water was deionized. Ferric chloride ($FeCl_3·6H_2O$), ferrous chloride ($FeCl_2·4H_2O$), sodium hydroxide (NaOH), isopropanol (C_3H_7OH), butanol (C_4H_9OH) and hexanol ($C_6H_{13}OH$) were analytical reagents. Span80 (sorbitan monooleate) and PS (petroleum sulfonate) were pure chemical, and kerosene was technical grade.

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2.2 Optimization of microemulsion system and preparation of Fe_3O_4 magnetic fluid

The dispersed water droplets in W/O microemulsion system were used as microreactors in this work. Through changing the mass ratio of surfactant, cosurfactant, aqueous and oil phase, different microemulsion systems were obtained. The systems were characterized by the transmittance measurements, and analyzed by the pseudoternary phase diagrams. The optimized system was thermodynamic stable and transparent.

The prepared sodium hydroxide aqueous stock solution, substituting for the dispersed water droplets, was solubilized to the optimized system under stirring. An aqueous solution containing ferrous chloride and ferric chloride (molar ratio = 2:1) was added dropwise into the microemulsion until pH value reached 11. After the solution was stirred for hours at a given temperature, a black Fe_3O_4 magnetic fluid was obtained.

2.3 Characterization

A model 721 spectrophotometer was used to determine the formations of microemulsion from transmittance measurement of the systems. Orion818 pH meter was used to detect the pH value of the whole system. The investigation of the stability and dispersity of magnetic fluid was carried out with an AxioCam HRO digital camera in Zeiss Axiovert 200M converted fluorescence microscope. A JEM-100CX II transmission electron microscope, operating at 100 kV, was used to observe particle size and its distribution of particles in the magnetic fluid. X-ray diffraction measurements were performed by a Rigaku Automated D/Max diffractometer at 50 kV 100 mV CuKα radiation with scanning speed 5°/min to check particle purity and crystalline structure. A high-speed centrifuge was used to test the stability of magnetic fluids at different rotating speeds.

Gouy magnetic balance was used to measure the magnetism of magnetic fluid. Magnetization of magnetic fluid can be calculated according to the formulas: $\chi = 2\Delta m\cdot g/H^2A$ and $M=\chi\cdot H$. Where $\Delta m = \Delta m_2 - \Delta m_1$, Δm_1 is the weight difference of a 20-cm long glass tube with 1.1 cm inner diameter in the presence and absence of the magnetic field, and Δm_2 is the weight difference of the glass tube and 12 cm high-magnetic fluid in the tube at same operation conditions, all measurements in the presence of the field were carried out along the ascending and descending directions of the applied magnetic field, respectively, in order to reduce the effect of remanence. Δm is the weight difference because of the magnetization of the sample. A is sectional area of the sample tube, H is intensity of the applied magnetic field, g is gravity constant, χ is magnetic susceptibility, and M is magnetization of the sample.

3 Results and discussion

3.1 Preparation of optimal microemulsion as a microreactor

Kerosene was used as the carrier liquid of the oil-based magnetic fluid and also the oil phase of microemulsion. Its theoretical HLB (hydrophilic and lipophilic balance) value is 6. In order to prepare stable microemulsion, the formula [10]: $HLB=HLB_1\times m_1+HLB_2\times m_2$ was used to determine the mass ratio of components in the mixed surfactant, where HLB_1 and HLB_2 were HLB values of components, m_1 and m_2 were their mass fraction, respectively. HLB value of Span80 is 4.3 and that of PS is 11.7; the evaluated mass ratio was 4:1.

The formed microemulsion regions of different ratio of mixed surfactant and cosurfactant were showed in Fig. 1. In the microemulsion systems consisting of Span80-PS, iso propanol, kerosene and water, the microemulsion regions would extend with the rising quantity of isopropanol. A greater region means larger water solubilization of microemulsion in such pseudoternary phase diagrams. All of them needed a high proportion of surfactant to reach their greatest solubilization of water. Normally, the microemulsion had gotten a bicontinuous structure in such state [11]. Theoretically, the greatest is the optimized one. Although the greatest microemulsion region occurred when the ratio of mixed

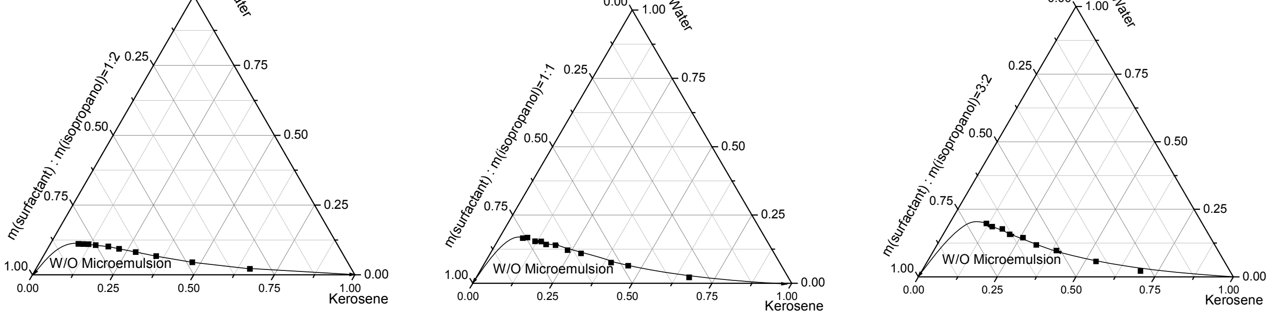

Fig. 1 Effects of surfactant and cosurfactant mass ratio on microemulsion formations

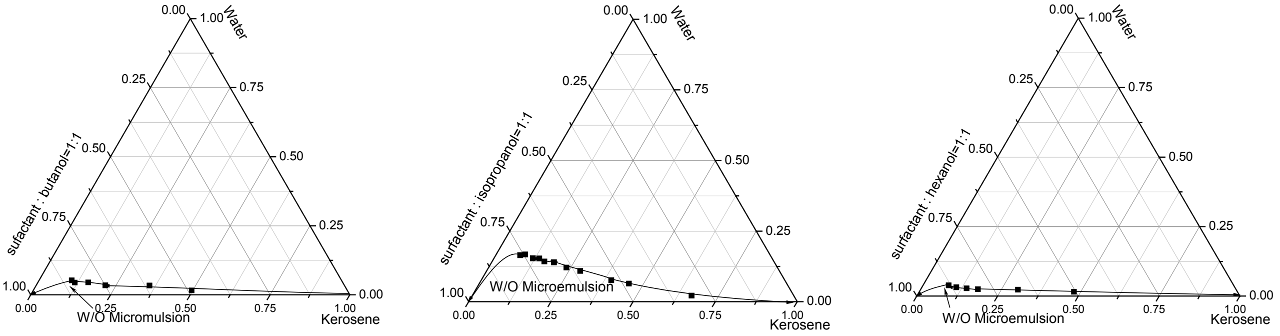

Fig. 2 Effects of the different cosurfactants on the formations of microemulsion

surfactant and cosurfactant was 3:2, the choice of 1:1 would save a lot of surfactant and cosurfactant because there was nearly no difference between 1:1 and 3:2 in most water solubilization.

The screen test of cosurfactants was carried out by drawing of the pseudoternary phase diagrams after the ratio of complex surfactant and cosurfactant was determined. As showed in Fig. 2, isopropanol, butanol and hexanol were chosen as cosurfactant candidates. Among the three, the microemulsion region was the largest when isopropanol was taken as cosurfactant. According to the geometry arrangement theory [12], the branched chain of isopropanol can increase the flexibility of oil-water interface and make it easy to curve. The branched chain also increases the tail group interfacial area. It makes the tail group significantly greater than the head group and the oil-water interface would protrude towards the oil phase, so there is a preferential formation of W/O microemulsion.

In brief, the W/O microemulsion consists of mixed Span80-PS (mass ratio = 4:1) as a complex surfactant, isopropanol as cosurfactant (mass ratio = 1:1 with the complex surfactant) and kerosene as oil phase.

3.2 Effects of molar ratio of Fe^{2+} and Fe^{3+} on magnetic particle synthesis

The water droplets in the microemulsion were taken as microreactors to accomplish the following precipitation reaction: $Fe^{2+} + 2Fe^{3+} + 8OH^{-} \rightarrow Fe_3O_4\downarrow + 4H_2O$. In such circumstances, the nano-scaled droplets limited the nucleus growth of Fe_3O_4 particles, and the presence of W/O interface avoided aggregation of particles when they collided, so that the particle size distribution was narrow. The surfactant molecules would passivate the particle surface immediately when they formed, and surfactant-coated magnetic particles could disperse stably in kerosene because of their lipophilic shell [13]. In such approach, it was unnecessary to separate magnetic particles from the reaction system and the oil-based magnetic fluid was prepared directly in one-step.

According to the above-mentioned chemical reaction equation, the stoichiometric ratio of Fe^{2+} and Fe^{3+} should be 1:2. But in consideration of the whole process carried out in the air, some Fe^{2+} must be oxidated; with the pre-experiment the molar ratio of Fe^{2+} and Fe^{3+} was determined to be 2:3 rather than 1:2. On the other hand, to make sure the crystalline formation of Fe_3O_4, the pH value of the reaction system was controlled at 11 [14].

3.3 Effects of reaction time and temperature on magnetic properties

The effects of reaction time on magnetic properties of Fe_3O_4 ferrofluid were showed in Fig. 3. At 30℃, the magnetization of magnetic fluid increased with enhancing of the applied magnetic field, the slopes of straight lines are the magnetic susceptibilities. From the insert of Fig. 3, the maximum magnetization occurred when the reaction time was 5 h in an applied magnetic field at 3,000 kA/m. The magnetization would descend if the reaction time was over 5 h because Fe^{2+} may be oxidized to Fe^{3+}, and other ferrites formed. Such ferrites would reduce the magnetic properties of magnetic fluid. Therefore the best reaction time was 5 hours.

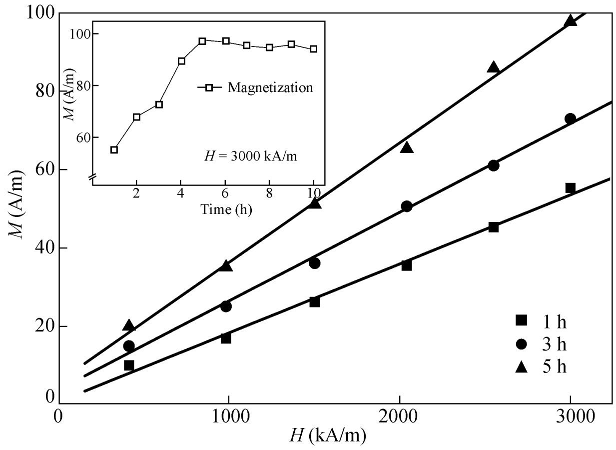

Fig. 3 Curves of magnetization of magnetic fluids for different reaction time at 30℃ versus applied magnetic field; the insert displays a curve of magnetization of Fe_3O_4 magnetic fluid versus reaction time at 30℃.

The effects of reaction temperature on magnetic properties of magnetic fluid were showed in Fig. 4. At 5-h reaction time the magnetization increased with enhancing the applied magnetic field. From the insert curve of Fig. 4, the maximum magnetization occurred when the reaction temperature was 30℃ with an applied magnetic field at 3,000 kA/m. The magnetization was almost linearly descendent if the temperature was over 30℃. It could be due to the high temperature destroyed the structure of microreactors, and the quality of particles can not be guaranteed. If the particle size was beyond the critical superparamagnetism size of Fe_3O_4, the phenomena that the magnetization increased with enhancing of the applied magnetic field would be inconspicuous [15]. The magnetization line of sample at 50℃ had proved it. With the increase in the temperature, the chance to synthesize other ferrite was also increased. It would reduce the magnetic properties as well. So the optimized reaction temperature was controlled at 30℃.

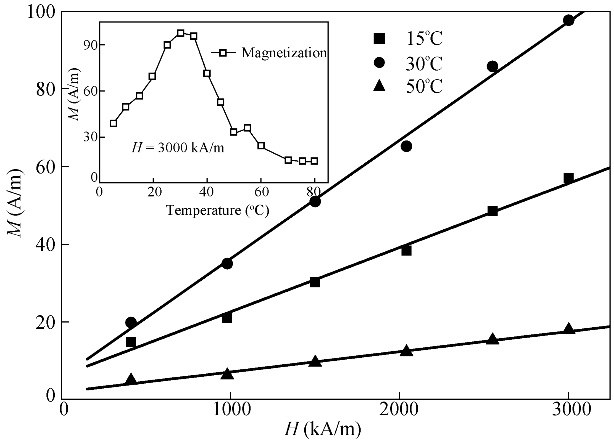

Fig. 4 Curves of magnetization of magnetic fluids for 5 h at different reaction temperatures versus applied magnetic field; the insert displays a curve of magnetization of Fe_3O_4 magnetic fluid for 5 h *vs* reaction temperatures

3.4 Stability of magnetic fluid

Through a separation test with a high-speed centrifuge both at 10,000 r/min for 20 min and at 2,000 r/min for 2 h, there was no sediment appeared of Fe_3O_4 magnetic fluid prepared at optimized reaction conditions. Standing of the magnetic fluid for 3 months at room temperature, there was no delamination and obvious precipitation. It indicated the magnetic fluid was stable. Why the electrolytes in magnetic fluid did not influence its stability is very interesting and significant, and this needs further research.

3.5 Characterization of magnetic fluid

Figure 5a is the digital photo (pixel 3900×3090) of the magnetic fluid. The Fe_3O_4 particles were dispersed well in the carrier liquid. Fig. 5b is the transmission electron microscopy photo of magnetic particles. It is showed that the average size of magnetic particles was about 10 nm with narrow size distribution.

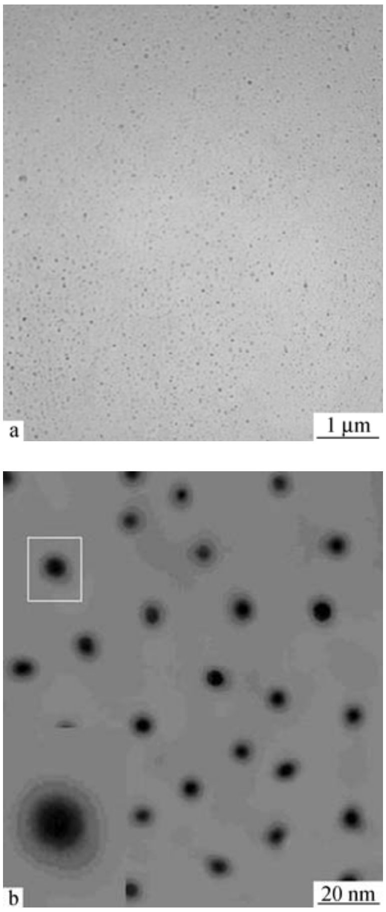

Fig. 5 a. Fluorescence Microscope Photo; b. TEM Photo

Figure 6 shows the XRD pattern of the synthesized Fe_3O_4 particles. There is only Fe_3O_4 to be detectable. It reveals the inverted spinel crystal structure. The increase of peak width indicates the effect of nano-scaled structure. With the XRD pattern, the average particle size can be evaluated from Debye-Scherrer equation $D=k\lambda/\beta\cos\theta$, where D is the average diameter of particles, θ is diffraction angle, λ is the wavelength of the incident X-ray, β is the half width of the maximal intensity peak, k donates *ca.* 1 at normal conditions [16]. The final result D=7.4 nm and this average diameter is an approximate value, it is a reference only. XRD and TEM results can prove each other well.

4 Conclusions

In this study, the pseudoternary phase diagram was used to determine the microemulsion components: the mass ratio of Span80-PS complex surfactant is 4:1; isopropanol is chosen as a cosurfactant, the mass ratio of surfactant and cosurfactant is 1:1. Taken the aqueous droplets prepared in the W/O microemulsion as microreactors to synthesize Fe_3O_4 nanoparticles, the optimized parameters are as follows: reaction temperature is 30℃, reaction time is 5 h, pH value is 11 and the molar ratio of Fe^{2+} and Fe^{3+} is 2:3. The synthesized particles have average diameter under 10 nm with narrow size distribution. The magnetic fluid has good magnetic properties. The whole technical process is greatly simplified compared with the traditional methods. It should be mentioned that there are electrolytes in the magnetic fluid from 'one-step method', but such impurities not be separated have nearly no effect on the stability and magnetism of Fe_3O_4 magnetic fluid. The magnetization of the magnetic fluid is not good as the reported magnetic fluids that are prepared by physical methods and organometallics thermolysis approach [17,18]. The reason is the concentration of Fe_3O_4 particles dispersed in the magnetic fluid is not high enough, so that the improving of microemulsion system would supply more microreactors to synthesize more magnetic particles, and the corresponding researches are undergoing.

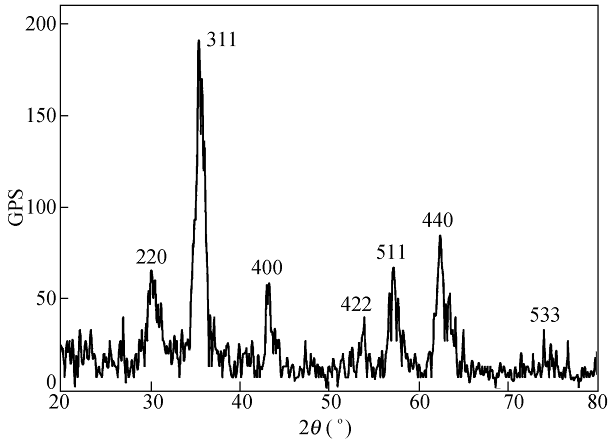

Fig. 6 XRD pattern of Fe_3O_4 particles of magnetic fluid

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