Magnetic Pickering Emulsions Stabilized by Fe$_3$O$_4$ Nanoparticles


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ABSTRACT: Superparamagnetic Fe$_3$O$_4$ nanoparticles prepared by a classical coprecipitation method were used as the stabilizer to prepare magnetic Pickering emulsions, and the effects of particle concentration, oil/water volume ratio, and oil polarity on the type, stability, composition, and morphology of these functional emulsions were investigated. The three-phase contact angle ($\theta_{ow}$) of the Fe$_3$O$_4$ nanoparticles at the oil—water interface was evaluated using the Washburn method, and the results showed that for nonpolar and weakly polar oils of dodecane and silicone, $\theta_{ow}$ is close to 90°, whereas for strongly polar oils of butyl butyrate and 1-decanol, $\theta_{ow}$ is far below 90°. Inherently hydrophilic Fe$_3$O$_4$ nanoparticles can be used to prepare stable dodecane—water and silicone—water emulsions, but they cannot stabilize butyl butyrate—water and decanol—water mixtures with macroscopic phase separation occurring, which is in good agreement with the contact angle data. Emulsions are of the oil-in-water type for both dodecane and silicone oil, and the average droplet size increases with an increase in the oil volume fraction. For stable emulsions, not all of the particles are adsorbed to drop interfaces; the fraction adsorbed decreases with an increase in the initial oil volume fraction. Changes in the particle concentration have no obvious influence on the stability of these emulsions, even though the droplet size decreases with concentration.

INTRODUCTION

Emulsions are widely used in many fields of daily life and in the food, cosmetic, pharmaceutical, paint, and petroleum industries. In an emulsion, one kind of liquid is dispersed in another kind of liquid in the form of droplets. Emulsifiers are required to prevent the coalescence of droplets and to obtain a stable system without macroscopic phase separation. Besides the commonly used amphiphilic molecules such as surfactants, emulsifiers can be nanometer- and micrometer-sized solid particles that adsorb at the liquid—liquid interface and form a protective film between the dispersed and continuous phases. The resultant solid-stabilized emulsions have been termed Pickering emulsions after Pickering’s early work in 1907. In the last two decades, solid particles as emulsion stabilizers have attracted much attention because of their irreversible adsorption, low toxicity, and low cost. Meanwhile, Pickering emulsions can be utilized to prepare porous materials, composite microspheres, and hollow microspheres because the special features of these emulsions are intimately related to the self-assembly of the particles themselves. In the case of solid particles, the three-phase contact angle at the oil—water interface, $\theta_{ow}$ is the key parameter determining the type and stability of the resultant emulsions. A value of $\theta_{ow}$ close to 90° is the most beneficial for particles to stabilize emulsions. For traditional emulsions, the size of the droplets can be below 0.1 $\mu$m, but for Pickering emulsions, the droplet size is frequently above 1 $\mu$m and sometimes in the millimeter range. Unlike traditional emulsions, Pickering emulsions are not always milky white but are sometimes black, gray, or reddish brown. A number of factors affect the stability and characteristics of Pickering emulsions, including the contact angle $\theta_{ow}$, the particle concentration, the size and shape of the particles, the oil type, the oil/water ratio, and the electrolyte concentration. Many studies have concluded that hydrophilic particles with $\theta_{ow} < 90°$ stabilize oil-in-water (O/W) emulsions, whereas hydrophobic particles with $\theta_{ow} > 90°$ stabilize water-in-oil (W/O) emulsions. However, not all particles can stabilize emulsions, and only when $\theta_{ow}$ is in a certain range can they act as efficient stabilizers. Kaptay predicted that the optimum $\theta_{ow}$ range is 70°–86° for stabilizing O/W emulsions and 94°–110° for stabilizing W/O emulsions. The oil type influences the preferred contact angle, with non-polar oils preferring O/W emulsions and polar oils preferring W/O emulsions. The addition of salt or surfactant to the system changes the charge and wettability of the particles. Other factors, such as the particle size and particle concentration, influence the size of the droplets in emulsions. For partially hydrophobic particles, the volume ratio of oil to water often

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determines the type of emulsion, and its variation can result in catastrophic phase inversion.25

During the self-assembly of particles for the preparation of functional materials, some functional particles were introduced to stabilize the emulsions, such as thermosensitive poly(N-isopropylacrylamide)-carrying particles,26 ethylcellulose,27 pH-sensitive hydroxyapatite,28 poly(4-vinyl pyridine)-SiO2 microparticles,28 and magnetic field-responsive paramagnetic particles.12 Melle et al.12 used carbonyl iron with a diameter of 1.1 μm to stabilize decane-in-water emulsions and investigated the influence of the magnetic field on the emulsion stability. The drops were millimeter in size, and upon applying an external magnetic field, they sedimented, distorted, and finally coalesced when the magnetic field intensity H was increased to above 86 kA/m. Kaiser et al.13 utilized polystyrene-brush-coated Fe3O4 to stabilize cyclohexane-in-water emulsions and found that after being heated in a magnetic field the emulsion is broken upon passing a critical temperature. Lan et al.29 synthesized bilayer oleic acid-coated Fe3O4 nanoparticles and used them to prepare pH-responsive Pickering emulsions. However, until now, no one has systematically investigated Pickering emulsions stabilized by unmodified Fe3O4 magnetic nanoparticles. Because of their outstanding magnetic properties and biocompatibility, Fe3O4 magnetic nanoparticles possess widespread application prospects in the biomedical fields of magnetic resonance imaging (MRI), targeted drug delivery, protein purification, and detection and magnetic damping.30–32

In general, the unmodified Fe3O4 magnetic nanoparticles are prepared by a classical coprecipitation method; therefore, there are many hydroxyl groups33,34 on the particle surface that make them hydrophilic. In this work, these hydrophilic Fe3O4 nanoparticles are utilized as the emulsifier and stabilizer to prepare novel magnetic Pickering emulsions, and the stability, composition, type, and morphology of these functional Pickering emulsions are investigated.

■ EXPERIMENTAL SECTION

Materials. The water used was purified by an Aquapro ultrapure water system (China), and its conductivity was 0.25 μS/cm as measured by the FE30/EL30 conductivity meter (Mettler-Toledo Instruments Co., Switzerland). FeSO4·7H2O (AR, 99%), FeCl3·6H2O (AR, 99%), NaOH (AR, 95%) were purchased from the Sinopharm Chemical Reagent Co. (China) and used as received. HCl (36–38%, AR), and NaOH (AR, 95%) were purchased from the Sinopharm Chemical Reagent Co., Switzerland. FeSO4·7H2O (AR, 99%), FeCl3·6H2O (AR, 99%), and NaOH (AR, 95%) were purchased from the Sinopharm Chemical Reagent Co. (China) and used as received. HCl (36–38%, AR), was obtained from Shanghai Lingfeng Chemical Reagent Co. (China) and used as received. In the preparation of magnetic Pickering emulsions, four oils of different polarity were chosen and used without further purification. These are 1-decanol (Sinopharm Chemical Reagent Co., AR 98%), dodecane (AR, 99%), 10 μL p-sodiumdodecylsulfonate PDM (AR, 99%), and butyl butyrate (AR, 99%) purchased from Aladdin Reagent Co. (China).

Synthesis of Fe3O4 Magnetic Nanoparticles. Fe3O4 magnetic nanoparticles were prepared by the coprecipitation of ferrous and ferric ions in an aqueous phase. Before preparation, a 0.5 mol/L FeSO4 solution with 0.2 mol/L HCl, a 1 mol/L FeCl3 solution with 0.2 mol/L HCl, and a 1.5 mol/L NaOH solution were prepared. During preparation, 100 mL of a NaOH solution was poured into a flask and heated to 80°C, and then the mixture of 10 mL of an FeSO4 solution and 10 mL of an FeCl3 solution was added to the flask dropwise in a N2 atmosphere and using an oil bath at 80°C. After the above mixture turned black, it was allowed to cool with continuous stirring, and then the resultant black particles were washed with water three times and dried in an LGJ-10 common-type freeze dryer (Beijing Huaxing Technology Development Co., China). The black particles (density = 4.25 g/cm3) obtained were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), photon correlation spectroscopy (PCS), and a vibrating sample magnetometer (VSM) to investigate their crystal structure, morphology, size distribution, and magnetic properties, respectively.

Preparation of Magnetic Pickering Emulsions. To investigate the effects of particle concentration, volume ratio of oil to water, and oil polarity on the stability, type, and morphology of the magnetic Pickering emulsions, three particle concentrations initially in water (0.5, 1, and 2 wt %), five volume fractions of oil (ϕo = 0.2, 0.4, 0.5, 0.6, and 0.8), and four oils with different polarity were utilized in this study. First, a certain mass of Fe3O4 nanoparticles and a certain volume of water were mixed and homogenized by a KQ100 ultrasonic cleaning machine (Kunshan Ultrasonic Instrument Co., China) using a power of 100 W for 1 h to prepare the aqueous dispersion. After the addition of a certain volume of oil, the magnetic Pickering emulsions were prepared using a high shear dispersing emulsifier (FM200, Fluko Equipment Shanghai Co., China) at a speed of 14 000 rpm for 3 min.

After preparation, the emulsions were poured into standard cylindrical sample bottles, and their stability was investigated by recording the change in height with time of the emulsion—aqueous-phase interface and then evaluating the volume fraction changes of the stable emulsion and resolved water. When no further changes occurred, photographs of the vessels were taken using a digital camera (Samsung S760). After this time, the separated aqueous phase was dried to weigh the remaining Fe3O4 nanoparticles, allowing the number of nanoparticles associated with the stable emulsion to be determined.

Measurements. The X-ray diffraction (XRD) pattern of the Fe3O4 nanoparticles was recorded by continuous scanning in the D8 Advance diffractometer (Bruker, Germany) with Cu Kα radiation (λ = 0.1541 nm) at room temperature. The measurements were performed at 40 kV and 20 mA from 10 to 90° with a 2θ scanning rate of 5°/min and a step of 0.02°. The resultant spectral pattern was compared with the standard pattern of Fe3O4 as a reference.

The morphology of the Fe3O4 nanoparticles was observed by TEM using a JEM-2100 microscope (JEOL, Japan) at an accelerating voltage of 200 kV. Before observation, the Fe3O4 nanoparticles were dispersed in water using a KQ100 ultrasonic cleaning machine with a power of 100 W for 1 h and then added dropwise to a carbon-coated copper grid. About 500 nanoparticles were observed to determine their average diameter.

The size and size distribution of the Fe3O4 nanoparticles were determined using PCS (Zetasizer Nano S, Malvern). The particles were first dispersed in water (0.1 wt %), and the measurement was made with a 4.0 mW He—Ne laser with a wavelength of 633 nm.

The magnetization curve of the Fe3O4 nanoparticle powder was obtained using a Lake Shore 7047 vibrating sample magnetometer at room temperature. The applied magnetic field was increased from 0 to 10 395 Oe, then reduced to —10 432 Oe, and then increased again to 10 764 Oe.

The emulsion type was determined by measuring its conductivity (FE30/EL30 conductivity meter). Generally if the conductivity is above 10 μS/cm, then the emulsion type is O/W, and if the conductivity is below 0.1 μS/cm, then the emulsion type is W/O.

An XPS-8C optical microscope (Yongcheng Optical Instruments Manufacturing Co., China) was used to observe the morphology of the emulsion droplets, and the images were collected by the digital image extracting equipment attached to the microscope. The size distribution of the emulsion droplets was estimated using an LS230 laser particle size analyzer (Beckman-Coulter, U.K.). Before the measurements, the emulsion was diluted 10-fold with pure water.

■ RESULTS AND DISCUSSION

Characterization of Fe3O4 Nanoparticles. There are many methods of preparing Fe3O4 magnetic nanoparticles, such as
coprecipitation, a hydrothermal process, microemulsion polymerization, and a high-temperature organic solvent method. The coprecipitation of Fe²⁺ and Fe³⁺ ions is one of the most convenient methods with low cost. During preparation, the mole ratio of Fe²⁺ to Fe³⁺, the pH of the aqueous phase, the crystallization temperature, and the crystallization time are important factors influencing the size and magnetic properties of the obtained Fe₃O₄ nanoparticles. In our experiment, a 20 mL solution of Fe²⁺ and Fe³⁺ was added to 100 mL of a NaOH solution, and the mole ratio of Fe²⁺ to Fe³⁺ is 1:2, exactly equal to that in the Fe₃O₄ structure.

The XRD pattern of the Fe₃O₄ nanoparticles is given in Figure 1a. The peak positions and intensities are in accord with the Fe₃O₄ diffractive data in the PDF card (19-0629) in soft MDI Jade 5. The characteristic diffraction peaks are located at 35.48, 62.62, 30.12, 57.02, and 43.12°, implying that the Fe₃O₄ nanoparticles possess typical inverse spinel structure.

Figure 1b,c shows the TEM image and the PCS size distribution of the particles, respectively. From the image, the apparent grain structure and aggregation of various sizes of the nanoparticles can be observed. The primary particle diameter is in the range of 15–35 nm. The light-scattering distribution is multimodal, with the first peak between 28 and 59 nm, the second peak between 91 and 342 nm, and the third peak between 342 and 1106 nm. The ratio of these three peaks is 17.2:52.4:30.5, and the peak tip positions are 43, 184, and 659 nm, respectively. The first peak represents the discrete particles, and the second and third peaks represent agglomerated particles.

The Fe₃O₄ nanoparticles have obvious superparamagnetism, as confirmed by Figure 1d. The response of the particles to a

*Figure 1. (a) X-ray diffraction pattern, (b) TEM image, (c) PCS size distribution, and (d) magnetization curve of the Fe₃O₄ nanoparticles.*
magnetic field is linear for some fields but no longer linearly proportional to the applied magnetic field at high fields because of the magnetization saturation. The saturation magnetization is 47.573 emu/g, the coercivity is 27.747 Oe, and the retentivity is 1.3981 emu/g. These data indicate that these Fe₃O₄ nanoparticles have little coercivity and very little retentivity.

**Evaluation of the Three-Phase Contact Angle \( \theta_{ow} \) of Fe₃O₄ Nanoparticles.** The three-phase contact angle \( \theta_{ow} \) of solid particles is an important parameter for estimating the stability and type of particle-stabilized emulsions. The coprecipitation of Fe²⁺ and Fe³⁺ in aqueous alkali renders the obtained Fe₃O₄ nanoparticles relatively hydrophilic (contact angle <90°). At present, many methods have been proposed to evaluate \( \theta_{ow} \) such as the sessile drop method, microcalorimetry, and the gel trapping technique. In our experiments, the Fe₃O₄ nanoparticles could not be pressed into a disk for sessile drop experiments. Here, we utilize a method similar to that described earlier employing Young’s equation (eqs 1–3) to calculate \( \theta_{ow} \) of the Fe₃O₄ nanoparticles. If a particle resides at the air–water surface, then the contact angle (measured in water) and the surface tension must satisfy eq 1. Likewise, if a particle resides at the oil–air surface then the contact angle (measured in oil) and the surface tension must satisfy eq 2. If a particle resides at the water–oil interface, then the contact angle (measured in water) and the interfacial tension must satisfy eq 3. In these equations, \( a \), \( o \), and \( w \) represent air, oil, and water, respectively, \( s \) represents solid particles, and \( \gamma \) represents the interfacial tension.

\[
\begin{align*}
\cos \theta_{ow} &= \frac{\gamma_{ao} - \gamma_{os}}{\gamma_{ow}} \quad \text{(1)} \\
\cos \theta_{ao} &= \frac{\gamma_{wa} - \gamma_{os}}{\gamma_{ao}} \quad \text{(2)} \\
\cos \theta_{ow} &= \frac{\gamma_{wa} - \gamma_{os}}{\gamma_{ow}} \quad \text{(3)}
\end{align*}
\]

When \( \gamma_{os} \) and \( \gamma_{ow} \) obtained from eqs 1 and 2 are introduced into eq 3, eq 4 can be obtained. Now \( \theta_{ow} \) of the Fe₃O₄ nanoparticles at the oil–water interface can be evaluated if the surface tension of the oil \( \gamma_{ao} \), the surface tension of water \( \gamma_{ow} \), the interfacial tension between oil and water \( \gamma_{ow} \), the contact angle at the air–water surface \( \theta_{ow} \), and the contact angle at the air–oil surface \( \theta_{ao} \) are known. Actually, \( \gamma_{ao} \) and \( \gamma_{ow} \) can be found in handbooks, \( \gamma_{ow} \) can be measured using a tensiometer, and \( \theta_{ao} \) and \( \theta_{ow} \) can be measured by the Washburn method.

\[
\cos \theta_{ow} = \frac{\gamma_{ow}}{\gamma_{ow}} \cos \theta_{ow} - \frac{\gamma_{ao}}{\gamma_{ow}} \cos \theta_{ao} \quad \text{(4)}
\]

The Washburn method is used to investigate the wettability of powdered and porous materials. It requires the measurement of the penetration rate of a liquid through a packed bed of powder/particles. Equation 5 shows how this is linked to the contact angle \( \theta \), where \( \Delta l \) is the penetration height, \( t \) is the penetration time, \( \beta \) is a material constant reflecting the number and orientation of pores in the powder, \( \gamma \) is the surface tension of the liquid, and \( \eta \) is the viscosity of the liquid. The contact angle obtained by this method is a relative value because the material constant \( \beta \) is unknown. However, if a perfect wetting liquid whose contact angle is zero can be found, then the most accurate value of the contact angle can be obtained because this method eliminates the effects of the flatness, porosity, and degree of packing of the solid particles.

\[
(\Delta l)^2 = \frac{\beta \gamma \cos \theta}{\eta} t \quad \text{(5)}
\]

In our work, the oil–water interfacial tension \( \gamma_{ow} \) is measured by the Wilhelmy plate method using a Krüss K100 fully automatic tensionmeter, and the penetration rate is measured with a JF99A powder contact angle measuring instrument (Powereach,
China). This instrument uses an air-pressure sensor to measure the penetration height of oil or water in the tube, and the corresponding principle can be described by eq 6, in which $\Delta P$ is the air-pressure variation and the other parameters have the same meaning as those in eq 5. In fact, $\Delta P$ varies linearly with $\Delta l$. When the surface tension $\gamma$ and viscosity $\eta$ of the liquid are known and $K \cos \theta$ is obtained from the experimental curve ($K$ is constant for a particular kind of particles and is proportional

Figure 3. Change in the volume fraction of the residual emulsion vs time for O/W emulsions stabilized by 1 wt % Fe$_3$O$_4$ nanoparticles initially in water with (a) dodecane, (b) 10 mPa s PDMS, (c) butyl butyrate, and (d) decanol.

Figure 4. Photographs of the vessels containing magnetic Pickering O/W emulsions stabilized by 1 wt % Fe$_3$O$_4$ nanoparticles initially in water taken 20 days after emulsion preparation. From left to right, $\phi_c = 0.2, 0.4, 0.5, 0.6, \text{ and } 0.8$: (a) dodecane, (b) 10 mPa s PDMS, (c) butyl butyrate, and (d) decanol.
to \( \beta \), the relative contact angle of many oils can be evaluated.

\[
(\Delta P)^2 = K \cos \theta \frac{\gamma}{\eta} t
\]

(6)

Table 4. Distribution of Particles in the Dodecane-in-Water Pickering Emulsions Stabilized by 1 wt % \( \text{Fe}_3\text{O}_4 \) Nanoparticles Initially in Water

<table>
<thead>
<tr>
<th>( \phi_o )</th>
<th>( m_{pv}/\text{g} )</th>
<th>( m_{pw}/\text{g} )</th>
<th>( m_{pt}/\text{g} )</th>
<th>( X/% )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.243</td>
<td>0.082</td>
<td>0.161</td>
<td>66.3</td>
</tr>
<tr>
<td>0.4</td>
<td>0.184</td>
<td>0.086</td>
<td>0.098</td>
<td>53.3</td>
</tr>
<tr>
<td>0.5</td>
<td>0.151</td>
<td>0.090</td>
<td>0.061</td>
<td>40.4</td>
</tr>
<tr>
<td>0.6</td>
<td>0.123</td>
<td>0.105</td>
<td>0.018</td>
<td>14.6</td>
</tr>
<tr>
<td>0.8</td>
<td>0.062</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5. Composition of the Dodecane-in-Water Pickering Emulsions Stabilized by 1 wt % \( \text{Fe}_3\text{O}_4 \) Nanoparticles Initially in Water

<table>
<thead>
<tr>
<th>( \phi_o )</th>
<th>( V_e/\text{mL} )</th>
<th>( \phi_{owe}/% )</th>
<th>( \phi_{we}/% )</th>
<th>( \phi_{oe}/% )</th>
<th>( \phi_{o}(100 \text{ mL}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>7.6</td>
<td>21.1</td>
<td>78.9</td>
<td>0.161</td>
<td>2.1</td>
</tr>
<tr>
<td>0.4</td>
<td>15.3</td>
<td>21.6</td>
<td>78.4</td>
<td>0.098</td>
<td>0.64</td>
</tr>
<tr>
<td>0.5</td>
<td>20.9</td>
<td>28.2</td>
<td>71.8</td>
<td>0.061</td>
<td>0.29</td>
</tr>
<tr>
<td>0.6</td>
<td>24.3</td>
<td>25.9</td>
<td>74.1</td>
<td>0.018</td>
<td>0.07</td>
</tr>
<tr>
<td>0.8</td>
<td>30.0</td>
<td>20.0</td>
<td>80.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6. Conductivity (in \( \mu \text{S cm}^{-1} \)) of the Pickering emulsions Stabilized by \( \text{Fe}_3\text{O}_4 \) Nanoparticles

<table>
<thead>
<tr>
<th>oil</th>
<th>( \phi_0 = 0.2 )</th>
<th>( \phi_0 = 0.4 )</th>
<th>( \phi_0 = 0.5 )</th>
<th>( \phi_0 = 0.6 )</th>
<th>( \phi_0 = 0.8 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>dodecane</td>
<td>0.5</td>
<td>22.8</td>
<td>19.2</td>
<td>17.2</td>
<td>13.4</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>25.0</td>
<td>19.9</td>
<td>17.8</td>
<td>16.2</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>32.7</td>
<td>22.4</td>
<td>19.0</td>
<td>16.6</td>
</tr>
<tr>
<td>PDMS</td>
<td>0.5</td>
<td>37.5</td>
<td>23.5</td>
<td>40.6</td>
<td>19.0</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>163.1</td>
<td>91.7</td>
<td>77.4</td>
<td>53.6</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>67.1</td>
<td>107.0</td>
<td>104.7</td>
<td>70.3</td>
</tr>
</tbody>
</table>

Here, four oils with different polarity were selected to evaluate \( \theta_{ow} \) of the \( \text{Fe}_3\text{O}_4 \) nanoparticles. Their polarity can be characterized by the intrinsic electric dipole moment \( \mu_0 \) and the dielectric constant \( \varepsilon \). Table 1 lists the values of these parameters, from which it can be deduced that dodecane is a nonpolar oil, hexamethyldisiloxane (HMDSO) is a weakly polar oil, and butyl butyrate and decanol are highly polar oils. (HMDSO was chosen instead of 10 mPa s PDMS because of its lower viscosity and higher tension; however, their structures are very similar.) The interfacial tensions between oil and water are given in Table 2. Using the Washburn method, when different oils and water are put in the container, the curves of the change in air pressure with time are obtained, as shown in Figure 2. Linear fits of the data between 20 and 100 s yield a value of \( K \cos \theta \) (with \( \theta \) being either \( \theta_{ao} \) or \( \theta_{aw} \)) when knowing the liquid viscosity and surface tension. The results are shown in Table 3, where it can be seen that the wettability of decanol on the particles was the best with the largest \( K \cos \theta \) value. If we can find a perfectly wetting liquid for the particles, we can deduce the packing parameter \( K \) and the absolute contact angle of all of the liquids. However, this is very difficult so we use this data in a comparative sense. By applying the values of the tension and \( K \cos \theta \) given in Tables 2 and 3, the values of \( \cos \theta_{ow} \) for dodecane, HMDSO, butyl butyrate, and decanol obtained from eq 4 are 71.71/\( K \), 105.0/\( K \), 204.0/\( K \), and 185.5/\( K \), respectively. By considering that \( \cos \theta_{ow} \approx 1 \) and \( \cos \theta_{ow} \) for dodecane is the smallest, we can deduce that the minimum value of \( K \) is 204.0 and \( \theta_{ow} \) for dodecane is closest to \( 90^\circ \). If we assume that \( \cos \theta_{ow} = 0.478 \) (when \( K \) is chosen as the minimum value of 204.0) for decanol, then \( \theta_{ow} \) of the \( \text{Fe}_3\text{O}_4 \) nanoparticles can be obtained (Table 3) by using eq 4 and the values in Table 2. It can be noted that for nonpolar oil dodecane, \( \theta_{ow} \approx 90^\circ \), suggesting that dodecane may be the best oil for preparing stable magnetic Pickering emulsions.

Stability of Magnetic Pickering Emulsions. In this study, dodecane, butyl butyrate, decanol, and a low-viscosity PDMS oil (with similar polarity and structure to HMDSO) were used as the oil phase to prepare magnetic Pickering emulsions. After preparation, the emulsions were kept at room temperature without stirring for 20 days. The changes in the volume fraction of the oil phase were monitored, and the conductivity of the emulsions was measured at different particle concentrations. The results are shown in Figure 5. Microscope images 20 days after the preparation of dodecane-in-water Pickering emulsions stabilized by \( \text{Fe}_3\text{O}_4 \) nanoparticles at different \( \phi_o \) values and particle concentrations: (a) 0.2, 1 wt %; (b) 0.4, 1 wt %; (c) 0.6, 1 wt %; (d) 0.8, 1 wt %; (e) 0.8, 0.5 wt %; and (f) 0.8, 2 wt %.

Table 4. Distribution of Particles in the Dodecane-in-Water Pickering Emulsions Stabilized by 1 wt % \( \text{Fe}_3\text{O}_4 \) Nanoparticles Initially in Water

Table 5. Composition of the Dodecane-in-Water Pickering Emulsions Stabilized by 1 wt % \( \text{Fe}_3\text{O}_4 \) Nanoparticles Initially in Water

Table 6. Conductivity (in \( \mu \text{S cm}^{-1} \)) of the Pickering emulsions Stabilized by \( \text{Fe}_3\text{O}_4 \) Nanoparticles

Figure 5. Microscope images 20 days after the preparation of dodecane-in-water Pickering emulsions stabilized by \( \text{Fe}_3\text{O}_4 \) nanoparticles at different \( \phi_o \) values and particle concentrations: (a) 0.2, 1 wt %; (b) 0.4, 1 wt %; (c) 0.6, 1 wt %; (d) 0.8, 1 wt %; (e) 0.8, 0.5 wt %; and (f) 0.8, 2 wt %.
residual emulsion and separated water phase are shown as a function of time in Figure 3. The volume fraction of the residual emulsion is acquired by dividing the height of the emulsion phase by the total height of the initial emulsion, and the volume fraction of the separated water phase is acquired by dividing the height of the lower aqueous phase by the total height of the initial emulsion. Because the initial particle concentration has no remarkable influence on the emulsion stability, the data of emulsions stabilized by 1 wt % Fe₃O₄ nanoparticles initially in water are shown as an example.

It can be seen that, except for the emulsions with φₒ = 0.8 containing dodecane or PDMS, which are completely stable, all other emulsions show an initial decrease in the residual emulsion fraction and an increase in the resolved water fraction with time before attaining subsequent stability. At about 500 min, the dodecane—water emulsions reach the stable state, but this occurs at about 1000 min in the PDMS—water case. However, butyl butyrate—water and decanol—water emulsions cannot reach the stable state and finally separate into two phases. It is evident that dodecane—water and PDMS—water systems can form emulsions stable to coalescence because of the protective film formed by Fe₃O₄ nanoparticles at the oil—water interface. This finding along with the inability of the same particles to stabilize butyl butyrate and decanol emulsions results in good agreement with the relative contact angle data given in Table 3. For dodecane and PDMS, their relative θₒw values are close to 90⁰, and for butyl butyrate and decanol, their relative θₒw values are far below 90⁰. For these relatively hydrophilic Fe₃O₄ nanoparticles, nonpolar and weakly polar oils are beneficial to the formation of stable Pickering emulsions. Moreover, the stable emulsion fraction increases with an increase in the volume fraction of oil. Such emulsions remain unchanged for at least 6 months. The sedimentation of excess particles in the water phase results in a color change in the emulsion from gray-black to gray-white.

This outstanding stability of these magnetic Pickering emulsions to coalescence and demulsification is due to the irreversible adsorption of the particles to droplet interfaces. The particle size is about 30 nm, the contact angle is close to 90⁰, and the water—dodecane interfacial tension is about 55 mN/m, which can be introduced into eq 7 to calculate the energy of detachment E of a single Fe₃O₄ nanoparticle. The calculated result is 1.74 × 10⁴ kT (k is the Boltzmann constant), confirming the strong adsorption of these particles in this case. However, for decanol and butyl butyrate, the value of (1 ± cos θₒw)² is much smaller, such that particles are not well held at their interfaces.

\[
E = \pi R^2 \gamma_{ow} (1 \pm \cos \theta_{ow})^2 \quad (7)
\]

Figure 6. Microscopic images 20 days after the preparation of PDMS-in-water Pickering emulsions stabilized by Fe₃O₄ nanoparticles with φₒ = 0.8 and different particle concentrations: (a) 0.5, (b) 1, and (c) 2 wt %.

Figure 7. Droplet size distributions 20 days after the preparation of dodecane-in-water Pickering emulsions stabilized by Fe₃O₄ nanoparticles: (a) size distribution for 1 wt % particles and different φₒ values and (b) mean droplet diameter vs φₒ from plot a.

The appearance of the vessels 20 days after emulsion preparation is given in Figure 4. For both dodecane and PDMS systems, the stability of the emulsion to creaming increases with the oil volume fraction. For butyl butyrate and decanol, extensive coalescence dominates the instability with a clear oil layer above the sedimented particle dispersion.

Composition Analysis of Magnetic Pickering Emulsions. In our experiments, we find that not all of the particles exist in the residual stable emulsions. The dodecane—water Pickering emulsions initially stabilized by 1 wt % Fe₃O₄ nanoparticles in water were used to investigate their composition further. The obtained experimental data are listed in Tables 4 and 5, where mᵢₒ is the original particle mass initially in water, mᵢₑ is the particle mass in the resolved aqueous phase, mᵢₚₑ is the particle mass in the stable
emulsion, \( X = m_{\text{Pe}}/m_{\text{Po}} \), is the weight fraction of particles required to stabilize the emulsion, \( V_e \) is the volume of the stable emulsion, \( \phi_{\text{oe}} \) is the actual volume fraction of water in the residual stable emulsion, \( \phi_{\text{oe}} \) is the actual volume fraction of oil in the residual stable emulsion, and \( \phi_p = m_{\text{Pe}}/V_e \) is the particle concentration in the stable emulsion.

The volume of the stable emulsion \( V_e \) increases with the volume fraction of oil, \( \phi_o \). For dodecane—water systems, almost all of the oil is in the form of droplets, and all of the emulsions become high-internal-phase emulsions (\( \phi_{\text{oe}} = 70–80\% \)), independent of the initial \( \phi_o \). This is one of the reasons that Pickering emulsions are used to prepare high-porosity materials.\(^{31,42}\) It is clear from Table 4 that not all the particles are adsorbed at the interfaces in emulsions. The weight fraction of particles (compared to the total amount) required for the stable emulsion is below 70% and decreases with an increase in \( \phi_o \). For \( \phi_o = 0.8 \), no water separates, so \( m_{\text{Pe}} \) cannot be measured.

**Type and Morphology of Magnetic Pickering Emulsions.**

The type of emulsion stabilized by Fe\(_3\)O\(_4\) nanoparticles can be determined from its conductivity. The measured conductivities of these emulsions are shown in Table 6. It can be seen that all of the emulsions have conductivity values larger than 10 \( \mu \)S/cm, indicating that both the water—dodecane and water—PDMS emulsions are O/W type. This was also confirmed by drop-test measurements.

Using optical microscopy and laser particle size analysis, we have determined the morphology and size of the emulsion droplets; see Figure 5 for dodecane and Figure 6 for PDMS. For the dodecane-in-water emulsions stabilized by 1 wt % Fe\(_3\)O\(_4\) nanoparticles, the average droplet size increases with an increase in \( \phi_o \) as shown in Figures 5 and 7. Because it was shown earlier that fewer particles are associated with the emulsion at higher \( \phi_o \), droplets coalesce to a greater extent (during the process of limited coalescence) until particle coverage is sufficient to halt it.

We have also investigated the influence of particle concentration on the droplet diameter of dodecane-in-water emulsions stabilized by Fe\(_3\)O\(_4\) nanoparticles (30 days after preparation), and these results are given in Figure 8. Apart from the low droplet size at 0.5 wt % particles, the average droplet size decreases with an increase in particle concentration as expected. The reason for the anomaly at 0.5 wt % is probably due to the change in the state of the particle dispersion in water with concentration; all particles are well dispersed at 0.5 wt %, but some aggregates are visible at higher concentrations. Because it has been shown that the droplet size of Pickering emulsions increases with particle size,\(^{24}\) this may be the origin of the peak in drop size seen in Figure 8.

**CONCLUSIONS**

Superparamagnetic Fe\(_3\)O\(_4\) nanoparticles prepared by a classical coprecipitation method were used as the stabilizer to prepare magnetic Pickering emulsions. By applying Young’s equation and using the Washburn method, the relative three-phase contact angle \( \theta_{\text{ow}} \) of the Fe\(_3\)O\(_4\) nanoparticles was evaluated for different oils. For nonpolar dodecane and weakly polar PDMS oils, the relative \( \theta_{\text{ow}} \) of the Fe\(_3\)O\(_4\) nanoparticles is closer to 90\(^\circ\), whereas for strongly polar butyl butyrate and decanol oils, the relative \( \theta_{\text{ow}} \) of the Fe\(_3\)O\(_4\) nanoparticles is far below 90\(^\circ\), which implies that for the hydrophilic Fe\(_3\)O\(_4\) nanoparticles, nonpolar and weakly polar oils are beneficial to the formation of stable Pickering emulsions. These results are in accordance with the experimental findings that Fe\(_3\)O\(_4\) nanoparticles can stabilize dodecane—water and silicone—water emulsions but cannot stabilize butyl butyrate—water and decanol—water mixtures. Not all of the particles are adsorbed to drop interfaces in the stable emulsions, and the fraction adsorbed at the interface decreases with an increase in the initial oil volume fraction. Emulsions are O/W for both dodecane and silicone oil, and the average droplet size increases with an increase in oil volume fraction and a decrease in particle concentration.

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