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Demulsification of Solids-Stabilized Emulsions Under Microwave Radiation

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Experimental data are presented to show the influence of solid particles on demulsification. It was found that the solid particles could effectively resist demulsification. Compared with conventional heating, microwave radiation can enhance the demulsification rate by an order of magnitude and increase the demulsification effectiveness. The demulsification effectiveness of the emulsions stabilized by graphite powder can reach 82%–89% in a very short time under microwave radiation, whilst that of the emulsions stabilized by barium sulfate can attain 100% under similar conditions.

Keywords emulsion, demulsification, microwave radiation

Introduction

Finely divided insoluble solid particles constitute an important class of emulsifier. The effectiveness of these solids in stabilizing emulsions depends on factors such as particle size, particle interactions, and wettability of the particles. Solids-stabilized emulsions are commonly encountered during the production of crude oil and synthetic fuels. Menon and Wasan reviewed the influence of contact angle, particle size, particle interactions, and surfactants on emulsion behavior (1). Tambe and Sharma reported that solid particles could stabilize emulsions both by providing steric hindrance to drop-drop coalescence and by modifying the rheological properties of the interfacial region (2). They had made significant advances in the study of the stability of colloid-stabilized emulsions (3–5). We presented the influence of alkyl metal phosphates, a Shengli resin fraction, and NaCl, on the shear viscosity of interfacial films and the stability of emulsions. It was found that the alkyl metal phosphates and the Shengli resin fraction

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could enhance the shear viscosity of interfacial films and the stability of emulsions. NaCl (0.01–0.03 mol/L) could change the shear viscosity of interfacial films containing alkyl metal phosphates and the Shengli resin fraction (6). Tsugita *et al.* investigated an oil-in-water emulsion system utilizing the characteristic of Na-Mont to form complexes with organic polar compounds (7). Neuhausler *et al.* reported that the emulsions were stabilized by particles in heterocoagulate cages surrounding the oil droplets (8). Midmore studied the effect of aqueous phase composition on the properties of a silica-stabilized water-in-oil emulsion (9). Binks described the preparation and properties of water-in-oil emulsions stabilized by nanometer-sized hydrophobic silica particles alone. Emulsion stability to sedimentation increases with particle concentration due to network formation of the particles in the continuous oil phase (10). Binks and Clint calculated oil-water contact angles for a solid of given hydrophobicity with a range of oils of different polarity utilizing a theoretical treatment developed by themselves (11). Binks and Kirkland utilized low temperature field emission scanning electron microscopy to visualize the interfacial structure of emulsions stabilized solely by solid particles (12). Arditty and Leal-Calderon indicated that the emulsion droplets coalesce was progressively reduced, if the total amount of particles was initially insufficient to fully cover the oil-water interfaces and the coalescence was halted with the increase of the degree of surface coverage by solid particles (13). Vignati and Piazza reported that the droplet interfacial tension was not modified by particle adsorption at the interface suggesting a purely steric stabilization mechanism. Surface roughness was shown to considerably lessen the ability of particles to stabilize droplets (14). Tarimala and Dai reported the fact that hydrophobic and hydrophilic solid particles could simultaneously assemble at the oil-water interface (15). Crude oil-brine emulsions constitute a special class of solids-stabilized emulsions, which has also been widely studied. These emulsions are ubiquitously present as stable water-in-oil emulsions in produced crude oil, as well as during oil spills (16–18).

For economic and operational reasons, it is necessary to separate completely the water from the crude oils before transporting or refining them. Minimizing the water levels in the oils can reduce pipeline corrosion and maximize pipeline usage (19–21). Microwave dielectric heating can dissipate heat inside the medium and raise the energy of the molecules rapidly. This heating mode is quite different from the conventional heating. By means of microwave dielectric heating, more molecules become energized, thus resulting in superheating and higher reaction rates (22, 23).

The concept of microwave demulsification was first introduced by Klaila (24) and Wolf (25) in their patent applications. Klaila conducted several other field tests after his patent was authorized, and the results were encouraging (26). Later, Fang *et al.* presented a demulsification model for 1:1 and 3:7 water-in-oil systems under microwave radiation. The experimental results showed that the percentage of water separated from the emulsions was higher than 80% under certain conditions (27). Liu compared microwave radiation demulsification with demulsification by gravity sedimentation, demulsification by chemicals, and demulsification by conventional heating. It was shown that the demulsification process was speeded up and the efficiency could be increased under microwave radiation (28).

The present study was conducted to examine the demulsification of solids-stabilized emulsions under microwave radiation. Our results showed that microwave radiation could enhance the demulsification rate by an order of magnitude and increase the demulsification effectiveness.

Experimental

Model System

The experiments in this work were performed using the following defined systems:

Aqueous phase: Double distilled water.

Oil phase: The *n*-decane used in this study was a chemical-grade reagent. The *n*-decane was obtained from Shanghai No. 1 Reagent Manufactory, China.

Surfactant: The stearic acid, A. R., was obtained from Haerbin Chemical Engineering and Science Reagent Plant, Heilongjiang, China.

Solid particles: The graphite powder, A. R., was obtained from Shenyang No. 2 Reagent Manufactory, Liaoning, China. The barium sulfate, A. R., was acquired from Tianjin No. 3 Chemical Reagent Manufactory, China.

Coloring matter: The coloring matter, methylene blue, was acquired from Guangzhou South Chemical Reagent Glasses Apparatus Ltd., Guangdong, China.

Preparation of Emulsions

Samples were prepared by using 1.5 mL double distilled water and 3.5 mL *n*-decane in a 10 mL test tube with a stopper (length 135.0 mm, diameter 15.5 mm). Stearic acid, as a surfactant, was dissolved in *n*-decane, and its concentration was 0.01 wt%. Solid particles of graphite powder or barium sulfate were added to the system. Their concentrations varied from 0.5 wt% to 2.0 wt%. The phases were mixed by a hand shaking motion 200 times at a frequency of roughly 2 times/sec. The photographs were taken immediately after the completion of the emulsions with a camera (made in Korea) installed on an optical microscope (made in China) at a magnification of 160 or 400. The nature of the emulsion (O/W or W/O) was established using methylene blue.

Demulsification

The demulsification experiments were performed by using either an oil-bath heating at 90°C or a microwave irradiation (850 w) at 2,450 MHz. The demulsification effectiveness was evaluated by measuring the emulsion volume as a function of time.

Results and Discussion

Figures 1 and 2 show the size of the graphite powder and barium sulfate, respectively. The size of the graphite powder is within the range of 0.5 to 2.5 μm and the particles are plate shaped. The barium sulfate is within the range of 0.2 to 0.5 μm and the particles are spheroidal in shape.

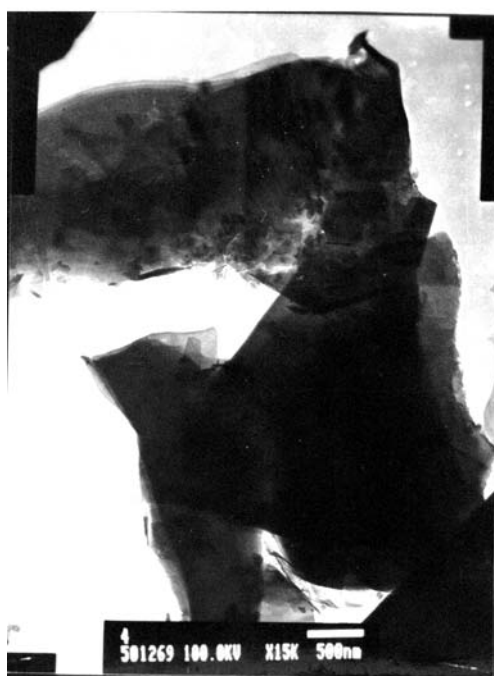
Figures 3 and 4 show, respectively, the droplet size of the emulsions stabilized by graphite powder and barium sulfate. The size of the emulsions stabilized by graphite powder is 350 μm or bigger, and the size of the emulsions stabilized by barium sulfate is 50 μm or bigger.

The results obtained from the demulsification experiments with conventional heating are shown in Figures 5 and 6. These data show the emulsion volume as a function of time.

It is found that graphite powder stabilizes water-in-oil emulsions and barium sulfate stabilizes oil-in-water emulsions. The nature of the emulsion (O/W or W/O) was established using methylene blue. In the absence of solid particles, no stable emulsions can be

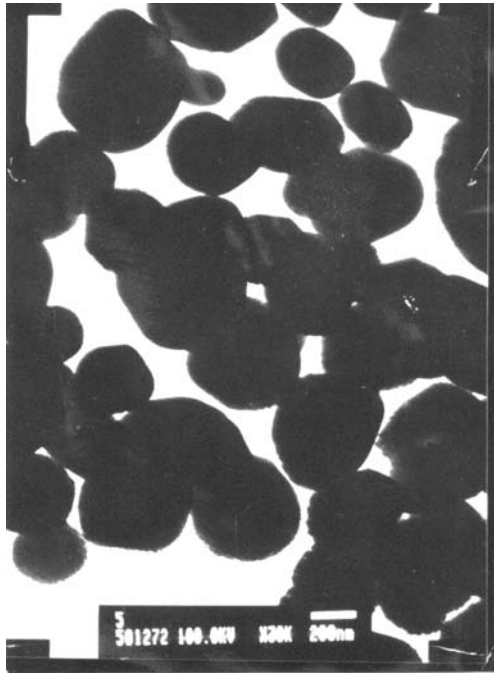


(a)

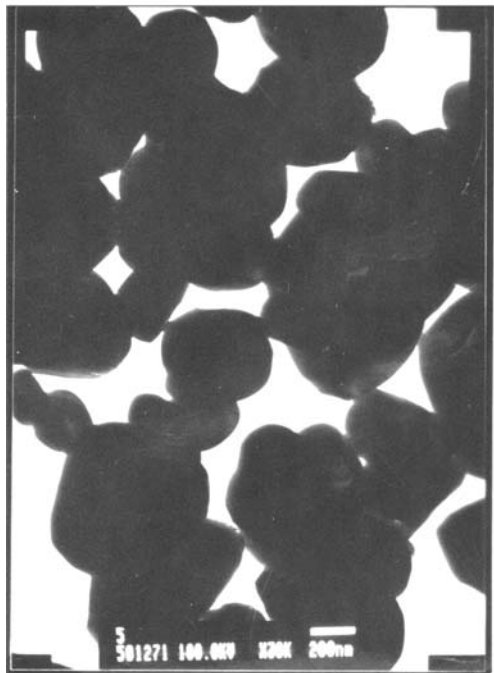


(b)

Figure 1. TEM photographs of graphite powder.

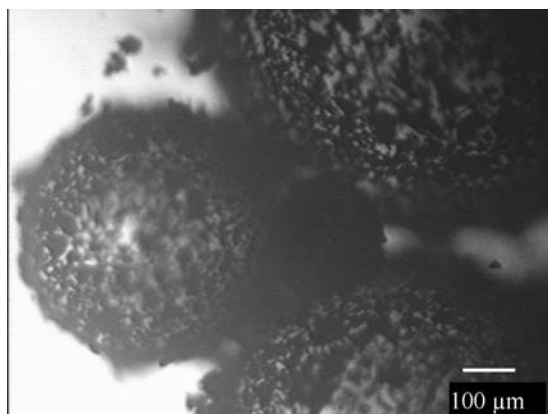


(a)

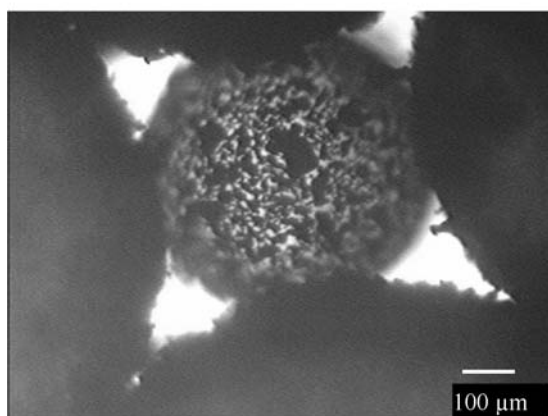


(b)

Figure 2. TEM photographs of barium sulfate.



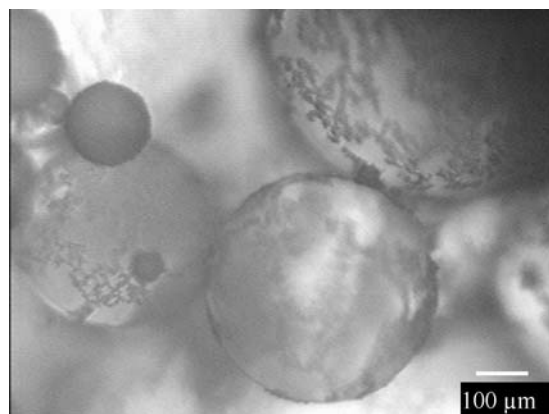
(a)



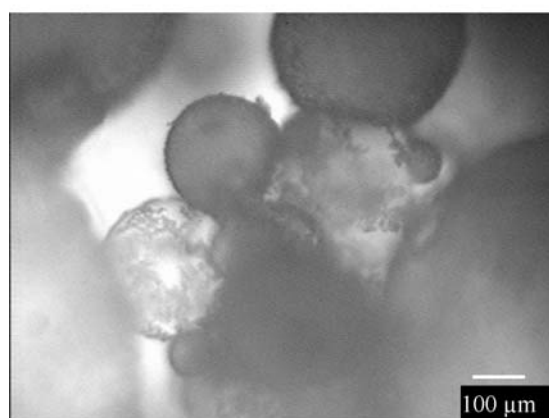
(b)

Figure 3. Optical microscopy photographs of the emulsions stabilized by 1.0 wt% graphite powder.

formed at a stearic acid concentration of 0.01 wt%. Stearic acid in the system is used as modifying the wetting properties of the solids, and probably enhancing the interparticle interactions as well (2). It is evident from these figures that the emulsion volume increases with the concentration of particles. For emulsions stabilized by graphite powder, the emulsion volumes decrease to 1.4 mL–2.1 mL at 0.5 wt%–2.0 wt% of graphite powder concentrations with the oil-bath heating at 90°C for 40 min (see Figure 5). The stabilization of solids-stabilized emulsions is mainly attributed to the mechanical resistance offered by the network of solids at the interface to drop-drop coalescence (see Figure 7). In addition to an electrostatic force, particles at the interface can also impart a certain degree of repulsion, and this will further enhance the stability of the emulsion (29). This increase in concentration of the particles at the interface can in turn lead to more stable emulsions. These results show that the effectiveness of solid particles in stabilizing emulsions depends on the complex structures formed by particles around the droplets, and on the degree of the particle interaction.



(a)



(b)

Figure 4. Optical microscopy photographs of the emulsions stabilized by 1.0 wt% barium sulfate.

The network structure of graphite powder (Figure 7(a)) is denser than that of barium sulfate (Figure 7(b)). It is due to the fact that the density of graphite powder (2.25^{15}) is smaller than that of barium sulfate (4.5^{15}), so the volume of graphite powder is greater than that of barium sulfate when they mass are equality. Furthermore, the average diameter of the water droplets of the emulsion stabilized by graphite powder is bigger than that of the oil droplets of the emulsion stabilized by barium sulfate, so the surface acreage of the water droplets of the emulsion stabilized by graphite powder is smaller than that of the oil droplets of the emulsion stabilized by barium sulfate (see Figures 3, 4, and 7).

Interestingly, when the concentration of barium sulfate was 0.5 wt%, the emulsion volume was 0 with the oil-bath heating at 90°C for 40 min. That is, the emulsion was completely demulsified. However, when the concentration of the barium sulfate varied from 1.0 wt% to 2.0 wt% the emulsion volumes varied from 0.4 mL to 0.5 mL under the same conditions (Figure 6). These results illustrate that a minimum concentration of particles

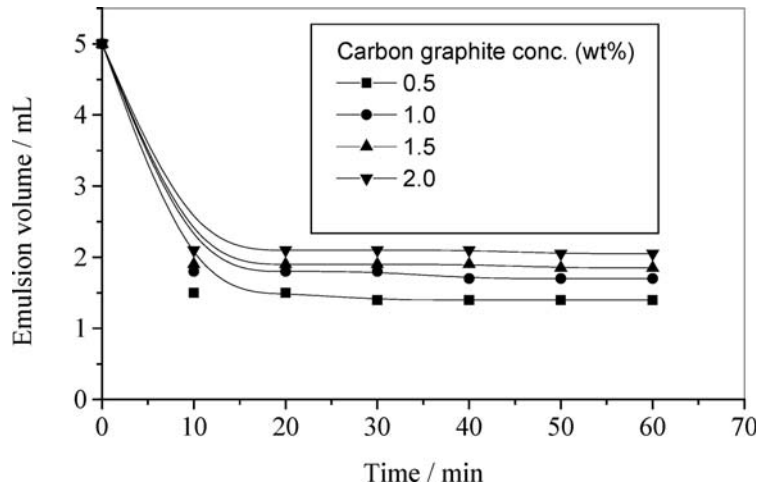


Figure 5. Demulsification of water-in-oil emulsion stabilized by graphite powder with conventional heating.

(minimum surface coverage) is required for any solids-stabilized emulsions. Only by increasing the particle concentration to a critical value can the network structure be formed, and the formation of the network is important for the stability of the emulsion.

The different effects shown by graphite powder and barium sulfate imply that the properties of the solid particles are very important in affecting the emulsion types and the demulsification effectiveness.

The microwave field effects on demulsification are plotted in Figures 8 and 9. For emulsions stabilized by graphite powder, the emulsion volumes decreased to 0.6 mL–0.9 mL at the graphite powder concentrations of 0.5 wt%–2.0 wt%, when using

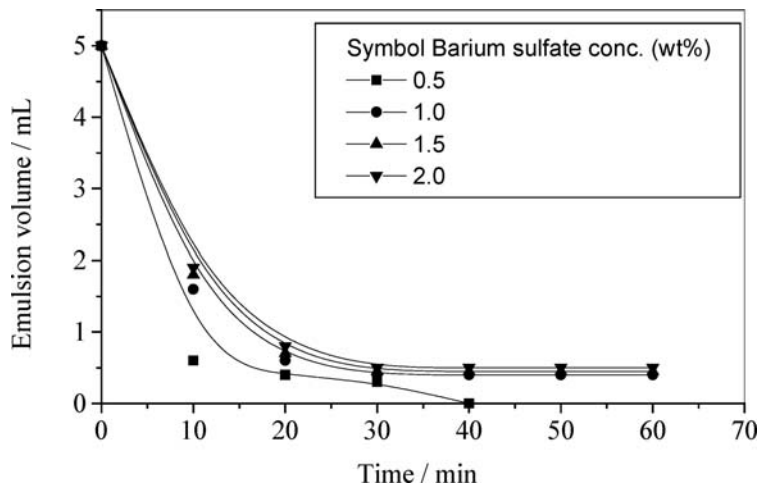
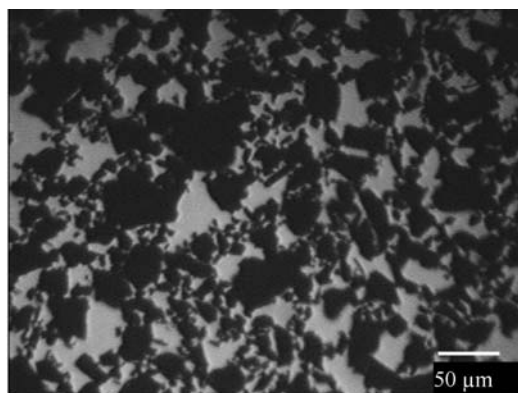
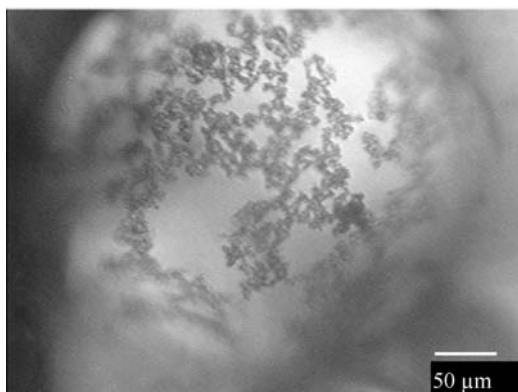


Figure 6. Demulsification of oil-in-water emulsion stabilized by barium sulfate with conventional heating.



(a)



(b)

Figure 7. Optical microscopy photographs of the surfaces of the emulsions. (a) Emulsion stabilized by 1.0 wt% graphite powder. (b) Emulsion stabilized by 1.0 wt% barium sulfate.

microwave irradiation for 5 min. Especially, for emulsions stabilized by barium sulfate, the demulsification efficiencies all attained 100% by using microwave irradiation for 5 min. The 0.5 wt%, barium sulfate stabilized system showed the fastest demulsification rate, and the emulsion was completely demulsified within 2 min. Comparing the data by conventional heating, microwave dielectric heating can enhance the demulsification rate by an order of magnitude and can thus increase the demulsification effectiveness. It is obvious that microwave radiation is a very effective method for demulsification of solids-stabilized emulsions. For water-in-oil emulsions stabilized by graphite powder, the dielectric constant and loss angle of water are greater than that of *n*-decane, so that water absorbs more energy than *n*-decane. Water droplets expand to make interface film thinner due to internal pressure. Consequently, the mechanical strength of the interface film becomes weaker, which in turn makes the interface film to be broken easier. For oil-in-water emulsions stabilized by barium sulfate, more water molecules become energized by means of microwave dielectric heating, which becomes weaker the particle interaction and makes the particles of the barium sulfate to disengage easier (22). Consequently, the

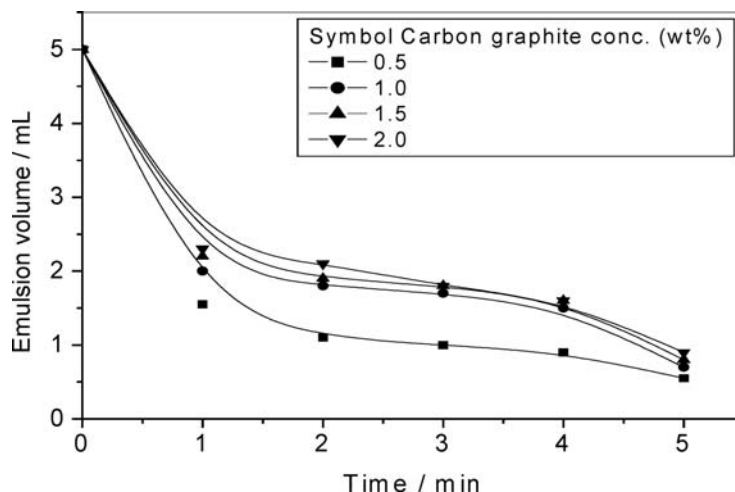


Figure 8. Demulsification of water-in-oil emulsion stabilized by graphite under microwave radiation.

network structure of the barium sulfate particles at the oil-water interface is disturbed. Without the support of network structure and the steric hindrance, the coalescence of liquid droplets could become easier. These effects made the emulsions easier to demulsify under microwave radiation.

Conclusions

The present investigation on the demulsification of solids-stabilized emulsions under microwave radiation has established that demulsification is accelerated significantly in a microwave radiation field as compared with the conventional heating method. It was

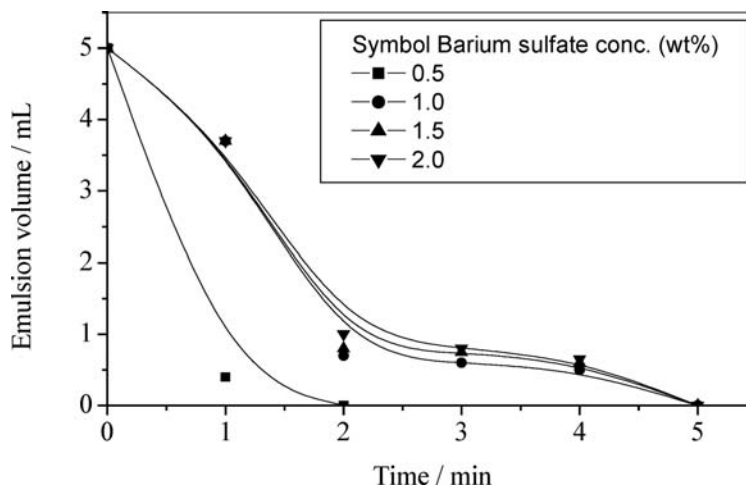


Figure 9. Demulsification of oil-in-water emulsion stabilized by barium sulfate under microwave radiation.

found that emulsions could be separated to oil and water in a very short time under microwave radiation. For emulsions stabilized by graphite powder, the minimum demulsification effectiveness was up to 82% in 5 min under microwave radiation. However, the maximum demulsification effectiveness was 72% with oil-bath heating at 90°C for 40 min. For emulsions stabilized by barium sulfate, the demulsification efficiencies all attained 100% in a very short time under microwave radiation. Consequently, microwave demulsification is advantageous for oil recovery processes, as well as for the reducing of waste generation.

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