Research Article

Fei Liu*, Yanling Wang, Xiaqing Li, Zhaoxiang Zhang, Xiaodong Dai, Xuewu Wang, Yanping Xin, Kun Liu, Liang Gao, Dehui Du, Chunyu Xing, Hong Jiang, and Zhihua Liu

The phase inversion mechanism of the pH-sensitive reversible invert emulsion from w/o to o/w

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Abstract: Alteration in the environmental conditions will cause a reversed reaction between o/w emulsion and w/o emulsion that has similar advantages of different liquids form on the reversible invert emulsion. The reversible phase inversion of the emulsion has a benefit of dealing with drilling cutting, so the reversible invert emulsion also can be thought used as a drilling fluid. The phase inversion from w/o emulsion to o/w emulsion can be divided into three stages. They are w/o emulsion, w/o/w emulsion, and o/w emulsion. In the w/o emulsion stage, the structure appeared among water droplets when the percentage of the HCl solution (5%) was less than 0.375%. In the w/o/w emulsion stage, the structure among water droplets existed at the beginning of this stage; however, the internal phase and the external phase can interchange their positions during the process. In the third stage, the structures among droplets of the emulsion would be broken and the degree of the dispersion of the oil droplet in the emulsion would increase. The changes in the microstructure, conductivity, electrical stability, standing stability, and the viscosity of the emulsion, which have edified among droplets in the process from w/o emulsion to o/w emulsion, were studied. The result of the microstructure microscopic observation agrees with the result of the electrical stability and viscosity experiments. Moreover, the internal phase and the external phase can interchange positions during the process.

Keywords: pH-responsive, phase inversion, microstructure

*** Corresponding author: Fei Liu,** School of Petroleum and Gas Engineering, Shengli College, China University of Petroleum, Dongying, Shandong 257061, P. R. China, e-mail: 865695501@qq.com
Yanling Wang: School of Petroleum Engineering, China University of Petroleum (East China), Qingdao, Shandong 266580, P. R. China
Xiaqing Li: Formation Damage Institute, Petroleum Engineering Technology Research Institute of Shengli Oilfield Company, Sinopec, Dongying, Shandong 257000, P. R. China
Zhaoxiang Zhang: Shandong Key Laboratory of Heavy Oil Production Technology, Petroleum Engineering Technology Research Institute, Shengli Oilfield Company Postdoctoral Research Station, Sinopec, Dongying, Shandong 257000, P. R. China
Xiaodong Dai, Xuewu Wang, Yanping Xin, Kun Liu, Liang Gao, Dehui Du, Chunyu Xing, Hong Jiang, Zhihua Liu: School of Petroleum and Gas Engineering, Shengli College, China University of Petroleum, Dongying, Shandong 257061, P. R. China

1 Introduction

An emulsion is a dispersed system wherein a liquid phase (also termed the internal or dispersed phase) is fragmented into droplets and suspended or dispersed in a second phase (termed the external or continuous phase) that is essentially immiscible in the first phase [1]. Most often, the emulsion is either water in oil emulsion (w/o) or oil in water emulsion (o/w), although more complex morphologies such as multiple emulsions can also be prepared under specific conditions [2–6]. Stability against coalescence is usually provided by an emulsifier [7,8]. The emulsifiers can be a molecular surfactant, solid particles, or a combination of surfactants and particles. Emulsions stabilized by surfactants are the most widely used emulsions [9].

The inversion of an emulsion, as the name implies, is a transition from one physical arrangement to another [10]. Flipping an emulsion from one type to the other is a difficult task. For instance, oil-based muds have complex w/o emulsions and are used as drilling fluids in oil and gas extraction to carry the drilling cuttings out of the well. For environmental reasons, cuttings must be separated from the mud and cleaned. Inverting the emulsion can certainly help to meet these requirements [11,12]. The understanding of the inversion process of the emulsions is thus of major importance in the oil industry. This practical example shows the importance of developing emulsion systems, which exhibit the appropriate emulsion type for a specific application. Experimentally, this can be suitably achieved by changing physicochemical parameters, referred to as field variables, such as temperature (ethoxylated emulsifiers are well known to be temperature sensitive), oil chain length, type or size of both the hydrophobic and hydrophilic moieties of the emulsifier, and electrolyte type and concentration [13–15].

The reversible invert emulsion [16–18], as the name implies, is an emulsion that can be reversibly inverted among different styles. The reversible invert emulsion can invert from w/o (o/w) emulsion to o/w (w/o) emulsion and vice versa. The reversible invert emulsion is one kind of invert emulsion, but the invert emulsion is not declared as a reversible invert emulsion. The reversible invert emulsion offers a possibility for the reusable working fluid that is environmentally suitable than the general working fluid. The working fluid used in the drilling as mentioned earlier is reversible invert emulsion, but only its first period is inverted from w/o emulsion to o/w emulsion. There are huge economic benefits and environmental benefits if it can be used as a reversible invert emulsion in the future [19].

Many studies have been done about the different types of reversible invert emulsions. The important reversible invert emulsions studied are pH-responsive reversible invert emulsion [20–25], temperature-responsive reversible invert emulsion [26], salt concentration-responsive reversible invert emulsion [27], light-responsive reversible invert emulsion [12], and emulsifier mixtures responsive reversible invert emulsion [28].

Arvind and Syed [20] discussed the systematic design, the development, and the testing of novel emulsifiers for innovative invert emulsion drilling fluids. The use of innovative emulsifier chemistry has produced novel invert emulsion fluids, which address the environmental and the performance and cost-related issues in drilling operations. Marchal et al. [26] described how a versatile amphiphilic diblock copolymer can form o/w or w/o emulsions depending on the pH and temperature. Binks and Jhonny [27] have studied the inversion of an emulsion stabilized solely by ionizable nanoparticles, whose type is simply affected by either a change in the pH or the salt concentration. Porcar et al. [12] found the light-induced control of the type (oil or water continuous medium) of emulsions stabilized by an appropriate combination of two polyelectrolyte surfactants. Binks and Lumsdon [28] studied the emulsions containing equal volumes of toluene and water stabilized by the nanometer-sized silica particles alone. It was observed that the transitional inversion, from o/w and vice versa, can be achieved by using a mixture of two particle types of different wettability. Also, most studies focus on the macroscopic properties and the factors affecting the reversible inversion of the emulsion [17,29–32]. However, the study of the change of the microstructure during a reversible inversion has not been exploited very much.

2 Materials and methodology

2.1 Materials

The deionized water was obtained through purifying water by an ion-exchange method. A hydraulic oil with a minimum kinematic viscosity of 4.14 $mm^2\,s^{-1}$ was used as the oil component of the invert drilling fluid. A primary alkyl amine surfactant was purchased from Jianglai Biological Technology Company and was used as received. Some amount of the diluted HCl was used in the experimental process (in a mass fraction of 5%).

2.2 Methodology

In this article, an experiment was performed to study the change of the emulsion microstructure during an inversion process from w/o to o/w of pH-sensitive reversible emulsion with structures among fluid droplets. A primary alkyl amine surfactant is used as an emulsifier, and the HCl solution (5%) and the NaOH solution (5%) are used as acid and alkali, respectively. First, the percentage of the HCl solution (5%) and the NaOH solution (5%) is determined as 1.0%, which can guarantee the reversible invention that happened for the reversible invert emulsion, which we know from the previous studies. The results obtained from the changing percentage of the HCl solution (5%) (under a stirring time of 5 min) and the stirring time (with a 5% of the HCl solution) can be used to draw a relationship between the changing microstructure during the inversion process. The macroscopic property of the emulsion-like conductivity measurements, electrical stability, viscosity, and emulsion stability was also analyzed with the result of the optical microscopic observations during the inversion process. Optical microscopy was used to see the difference between the emulsion's microstructure after adding a different percentage of the HCl solution and the different stirring time. The inversion process during which the microstructure of the emulsion would change from w/o emulsion to w/o/w emulsion and finally change into o/w emulsion at the end of this process can be seen. Thus, studying the change of the microstructure of the pH-sensitive reversible emulsion, in which structure exist among droplets, near the phase inversion point from w/o to o/w.

2.3 Characterization of emulsion

2.3.1 Conductivity

The conductivity of the emulsions was measured using a digital conductivity meter immediately after preparation. The emulsions were classified according to their conductivities. A high conductivity indicated an o/w emulsion or w/o/w emulsion, and a low (immeasurable) conductivity (<1 μS cm^{-1}) indicated a w/o emulsion or o/w/o emulsion. These results were confirmed using the "drop test," in which a drop of a water-soluble (or oil-soluble) dye was added to the emulsion, and its ease of dispersion was monitored by visual inspection. Relatively rapid dispersion indicated that the continuous phase of the emulsion was the same as the diluent (either water or oil).

2.3.2 Optical microscopy

A drop of the diluted emulsion was placed on a microscope slide and viewed using an optical microscope fitted with a digital camera. This technique was used to observe the microstructure of emulsion.

2.3.3 Electrical stability

Electrical stability was measured by an electrical stability tester, which is used mainly to measure the relative stability of w/o emulsion. Water is not continuous in a w/o emulsion, and the voltage would keep rising until the emulsion is broken and that the current could be measured. On the contrary, the water is continuous in the o/w emulsion and the current could be measured at a very low voltage. High electrical stability measured number means high stability of the emulsion. The style of the emulsion also can be measured by electrical stability.

2.3.4 Viscosity

Viscosity was measured by the viscometer. The viscosity represented the closeness of the structure among droplets. The change of the microstructure observed should agree with the changing trend of the viscosity. The viscosity and the microstructure of the emulsion were used to infer the change during the phase inversion of the reversible invert emulsion.

2.3.5 Emulsion stability

The emulsion was transferred into a stoppered glass tube with an internal diameter glass diameter of 2 cm and a length of 19 cm to observe the phase behavior of the dispersions 24 h after preparation at 25°C. The bottom of the vessels also could not be seen clearly from a normal photograph and need light behind the vessels to help vessels be seen clearly. The stability of the emulsions to creaming and coalescence was assessed by monitoring the positions of the water–emulsion and emulsion–oil interfaces, respectively, with time [33].

3 Results and discussion

3.1 Performance of the reversible invert emulsion fluids

The reversible invert performance was conducted through the distribution test, the conductivity experiment, and the electrical stability experiment. The initial w/o emulsion have high electrical stability of 130 V, after treating the w/o emulsion with HCl solution, it inverts successfully into an o/w with a conductivity of 80 μS cm^{-1} and an electrical stability of 1 V, after adding 1% NaOH solution to the o/w emulsion, it was observed

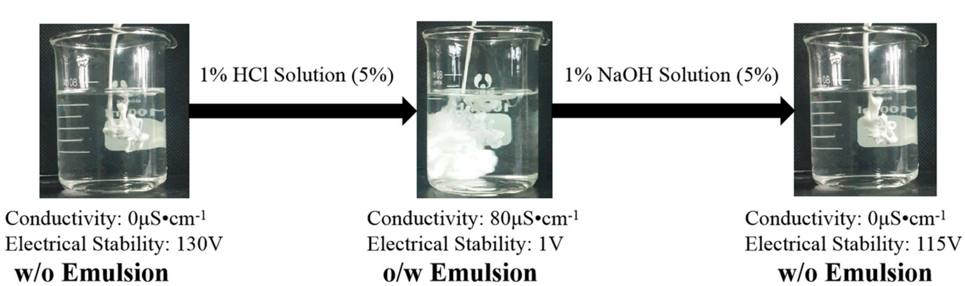

Figure 1: Reversible invert performance test result.

that the emulsion inverts into a w/o emulsion with the electrical stability increased from 1 to 115 V and the conductivity also reduced from 80 to 0 μS cm^{-1}. This process is demonstrated in Figure 1.

3.2 The change of microstructure of reversible invert emulsion during w/o to o/w

The phase inversion point was known by the change in the conductivity and electrical stability of the emulsion when the stirring time was kept at 5 min during the experiment (Figure 2). The emulsion was still w/o emulsion when the percentage of the HCl solution is 0.3625 because the conductivity and the electrical stability were 0 μS cm^{-1} and 151 V, respectively, at that instance. The emulsion will become o/w emulsion when the percentage of the HCl solution (5%) is 0.375% because the conductivity and the electrical stability are 2 μS cm^{-1} and 1 V, respectively.

From Figure 2, it was observed that the w/o began to change into an o/w emulsion when the percentage of the HCl was more than 0.375%. The viscosity of the emulsion, when the percentage of HCl was 0.375%, increased sharply and decreased during this process. The change of w/o emulsion to o/w emulsion process of the reversible inversion emulsion can be divided into three stages relying on the result of the following studies below.

3.2.1 The first stage of the inversion process – w/o emulsion

The change of the emulsion microstructure following the change of the HCl solution (5%) adding percentage was studied (under a stirring time 5 min) in the first stage (Figure 3). There are structures among droplets when the percentage of the HCl solution (5%) is less than 0.375%. The closeness of the structure among droplets would first increase and then decrease following the increase of the percentage of the HCl solution (5%), and the most closed structure among water droplets emerged at the point when the percentage of the HCl solution (5%) is 0.2% (Figure 4). The result of the microstructure observation agrees with the result of the viscosity experiment. Also, the water droplet size would first decrease and then increase following the increasin of the percentage of the HCl solution, and the overall least water droplet size emerged at the point when the percentage of the HCl solution is 0.2%. The electrical stability number also has a tendency that first increasing and then decreasing follow the increase of the percentage of the HCl solution, and the highest electrical stability number emerged at the point that the percentage of the HCl solution is 0.2% (Figure 2), which means the droplets of the emulsion have overall least volume at this point. The result of the microstructure observation agrees with the result of the electrical stability experiment.

It was also observed that the adding percentage of the HCl solution increasing, cause the tightness of the structure among the water droplets in the w/o emulsion firstly rise and then fall down. The same action was observed in terms of the stability of the structure among the water droplets (Figure 5). The volume of the upper oil first decreased and then increased. More amount of the upper oil was observed at the point when the HCl solution is 0.2%. The resultant microstructure agreed with the changing trend of the volume of the upper oil. Furthermore, no bottom water was observed at this stage, which infers that the stability of the

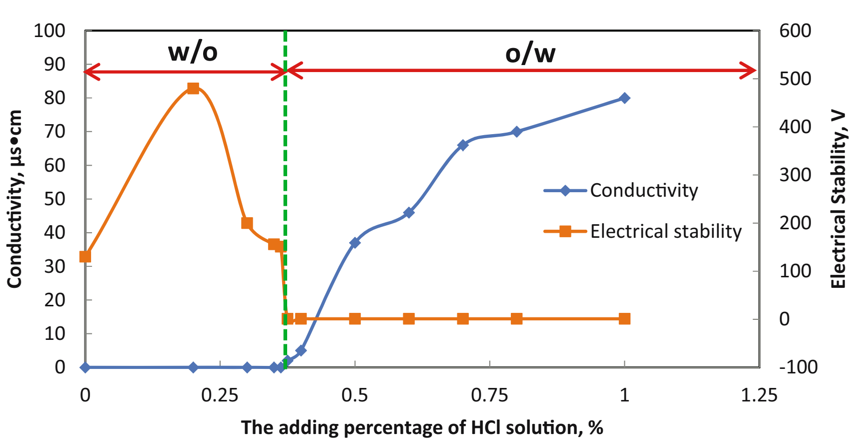

Figure 2: The relationship among the conductivity, the electrical stability, and the percentage of HCl solution (5%).

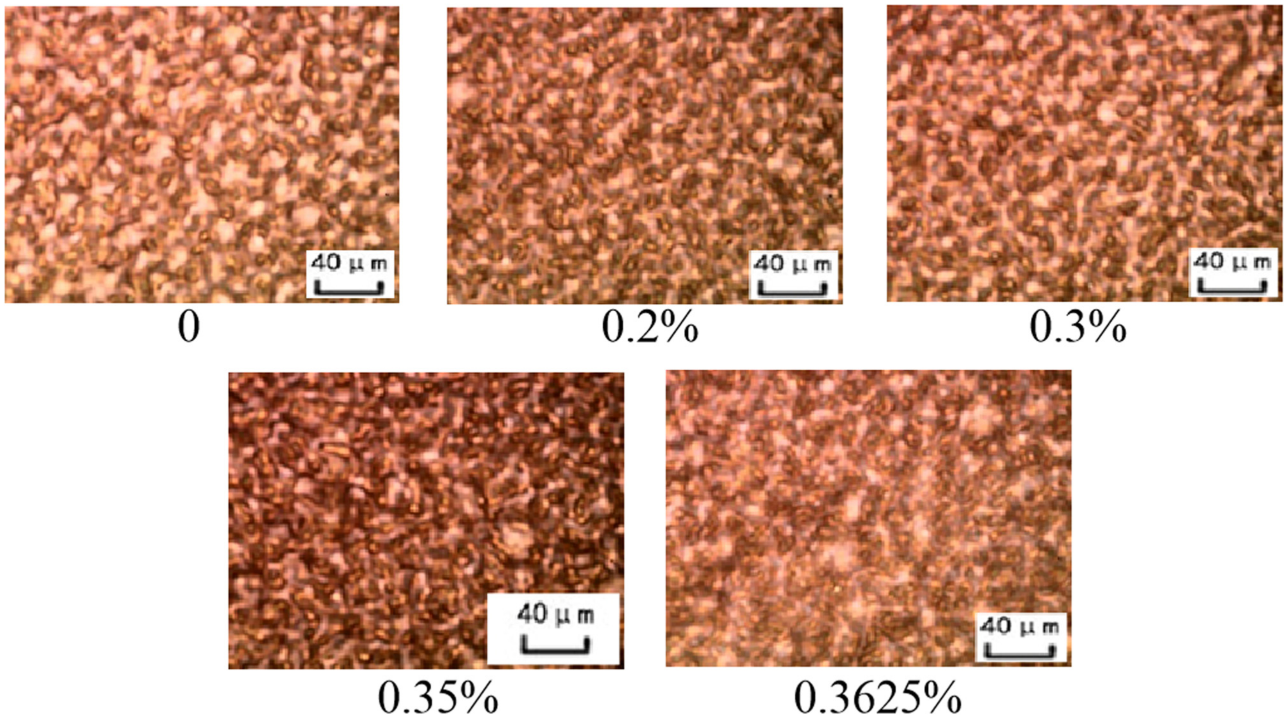

Figure 3: The relationship among the microstructure and the percentage of HCl solution (5%; less than 0.3625%) in the first stage of the process – w/o emulsion.

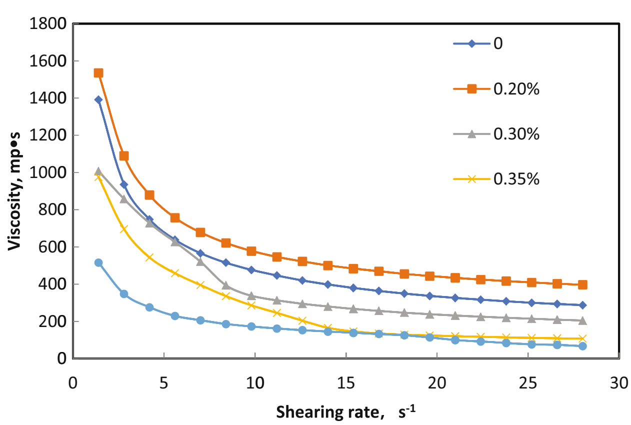

Figure 4: The relationship among the viscosity, the shearing rate, and the percentage of the HCl solution (5%; less than 0.3625%).

emulsion is so good that the water droplets were still intact after 24 h.

3.2.2 The second stage – w/o/w emulsion

The structure still exist among the water droplets in the emulsion system at the beginning of this stage, the water droplet in the oil phase coalesced into continuous phase and breaking the continuous oil into oil droplet following an increase in the stirring time. The internal phase and the external phase interchanged positions during the process. The oil droplet size became less as the stirring time was increased. The w/o/w emulsion would change into o/w emulsion at the end of this stage.

The style of the emulsion was w/o/w emulsion when the stirring time is 5 s. The structure among the water droplets in the w/o emulsion is very tight and hard to be broken, so the structure also exist among the water (w_2) droplets in the $w_2/o/w_1$ emulsion (Figure 6). After stirring for 5 s, it was observed that the emulsion moved into a transition state, which is very unstable. The coalescence between the droplets was observed through the change in the image of the emulsion microstructure under a microscope (Figure 7). The viscosity of the emulsion dropped due to the coalescence caused by easily breaking the water droplets. The viscosity of the freshly prepared emulsion and the emulsion standing for 1 h agreed to the phenomenon that the coalescence of the oil droplets can be easily broken during the standing process (Figure 8).

Second, the oil droplets with different kinds of microstructures coexisted in the emulsion because the emulsion was in the transitional zone. The microstructure was same at a stirring time of 10 and 15 s. When stirred for 20 s, the large oil droplets were separated into

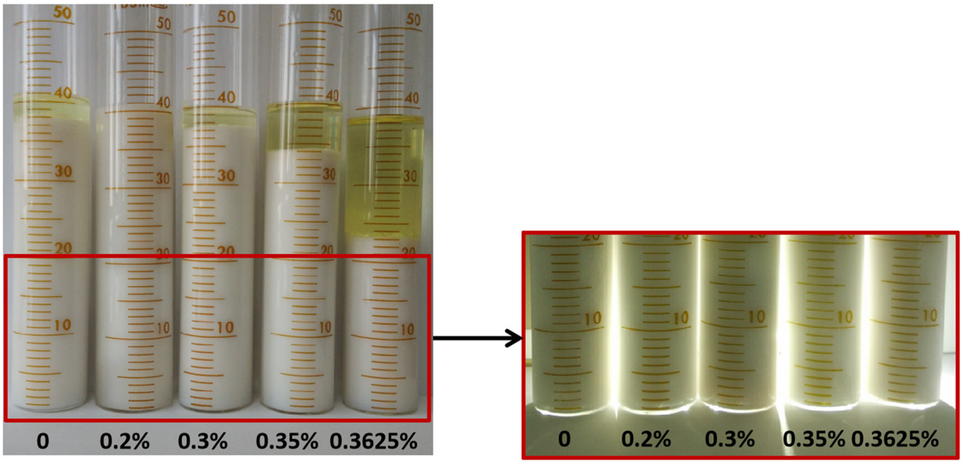

Figure 5: Photograph of emulsions with different percentages of the HCl solution (5%; the percentage is from 0 to 0.3625% and the stirring time is 5 min) after 24 h of preparation.

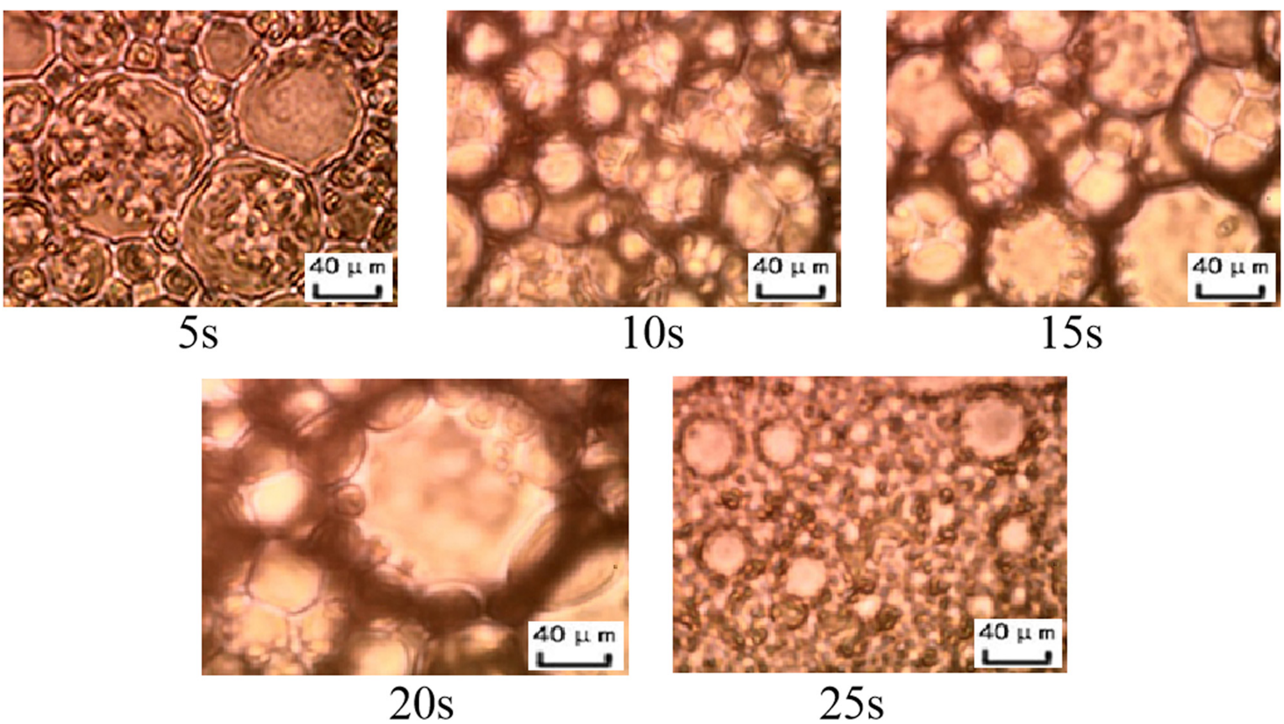

Figure 6: The relationship between the microstructure and the percentage of HCl solution (5%; the percentage of the HCl solution (5%) is 0.375%) in the second stage of the process—w/o/w emulsion.

smaller oil droplets with continuous water phase. Different kinds of oil microstructure existed in the emulsion in the transition zone (Figure 9).

Finally, the o/w emulsion had a structure among the oil droplets when the stirring time was 25 s. The structure was unstable and broke down after standing for a 1 h (Figure 6). The viscosity of the emulsion declined during the standing agreed with the phenomenon that the structure among oil droplets was broken during the standing procedure.

3.2.3 The third stage – o/w emulsion

The final stage of the inversion can be divided into two processes. In the first process, the structure among droplets

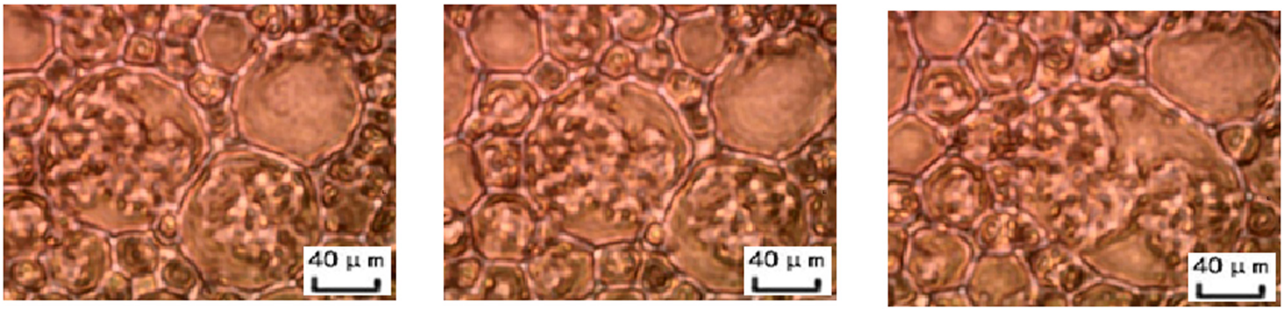

Figure 7: The change of the microstructure image of the emulsion after 5 s stirring (the percentage of the HCl solution (5%) is 0.375%) during 1 h standing.

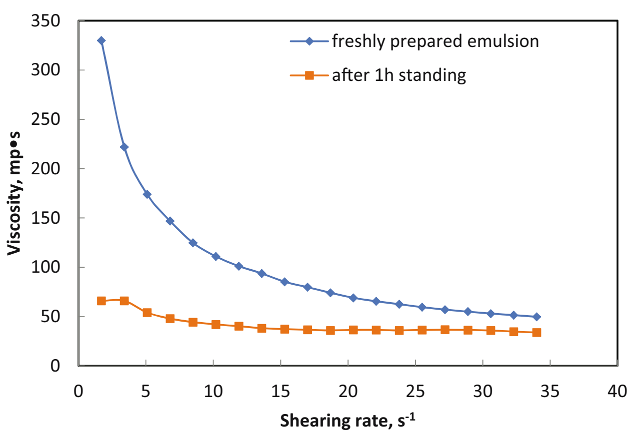

Figure 8: The contrast of the viscosity of the emulsion after 5 s stirring (the percentage of the HCl solution (5%) is 0.375%) between freshly prepared emulsion and 1 h later.

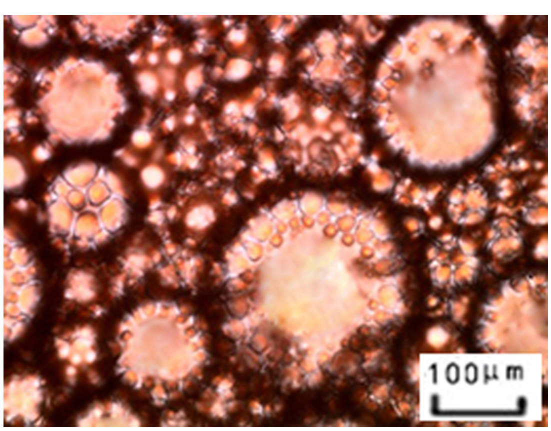

Figure 9: The microstructure of the emulsion (the percentage of the HCl solution (5%) is 0.375% and the stirring time is 20 s).

of the emulsion would be broken following an increase of the stirring time. It was observed that the dispersion of the oil droplet in the emulsion would become better (Figure 10). The conductivity of the emulsion increased due to the broken structures among the droplets of the emulsion (Figure 11). The broken structures caused a continuity in the water phase of the emulsion. Also, the viscosity of the emulsion dropped following the breaking of the structure among the water droplets (Figure 12). The results obtained at this stage agreed with the results of the conductivity experiment and viscosity experiments.

The second part of the final stage was characterized by a drop in the viscosity at the beginning. The viscosity then increased following an increase in the changing trend in the volume of the droplets of the emulsion. The minimum viscosity also emerged at the point when the HCl solution is 0.4% (Figure 13). The probability of collision among water droplets increased when the water droplet becomes bigger and the viscosity of the emulsion increased in this process (Figure 14). The conductivity of the emulsion increased slowly because of the increasing ion concentration due to the increase in the percentage of the HCl solution.

The stability of the emulsion was conducted by monitoring for 24 h after mixing with different percentages of HCl solutions (Figure 15). With the increase in the percentage of the HCl solution, there was no upper oil at the beginning of this period (the HCl solution between 0.375% and 0.7%) because of the high stability of the oil droplet. The upper oil emerged when the HCl solution is more than 0.8% due to the increasing oil droplet size. The results of the microstructure observation agreed with the changing trend of the volume of the upper oil.

3.3 pH sensitivity characterization

The pH of the emulsion was different at different percentages of the HCl solution (Figure 16). When the HCl solution is more than 0.375%, the emulsion system was observed in an acidic medium and the emulsifier existed as an oil-in-water emulsifier, which could stabilize the oil-in-water emulsion. When HCl was less

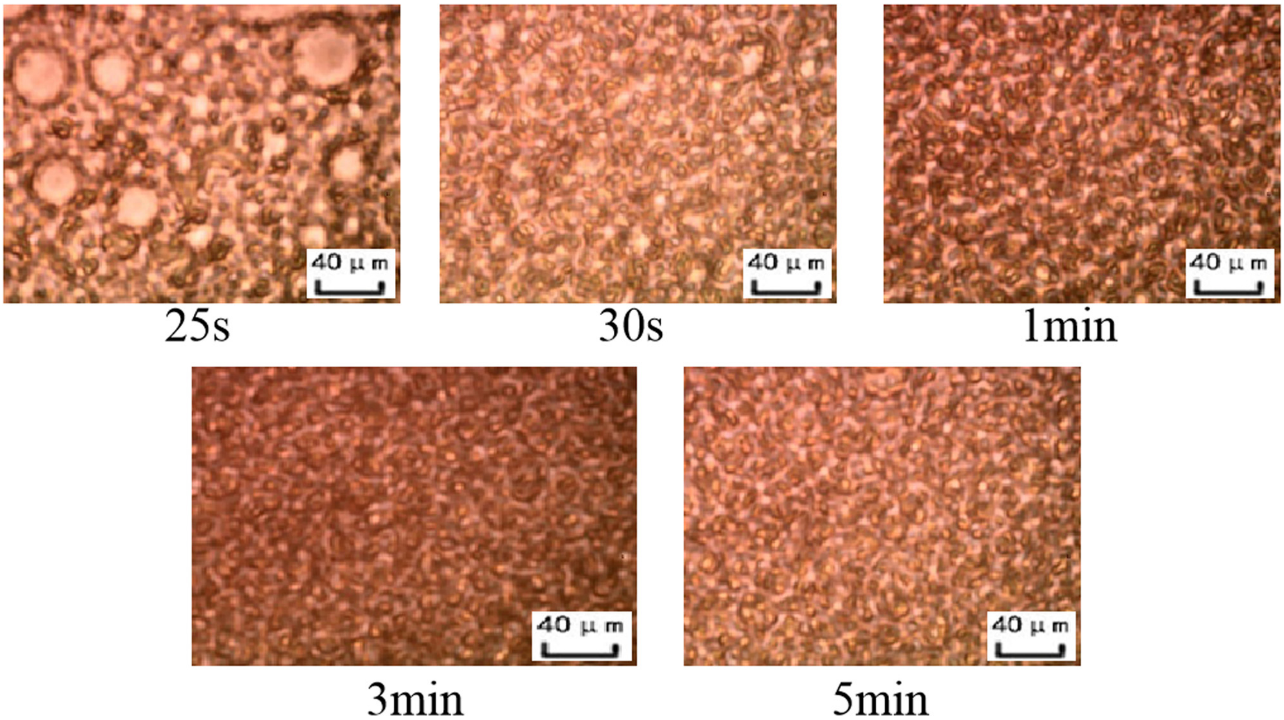

Figure 10: The relationship between the microstructure and the stirring time (the percentage of the HCl solution (5%) is 0.375% and the stirring time is between 25 s and 5 min).

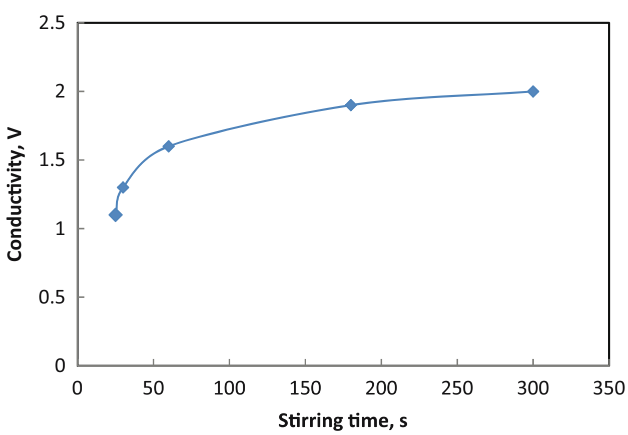

Figure 11: The relationship between the conductivity and the stirring time (the percentage of the HCl solution (5%) is 0.375%).

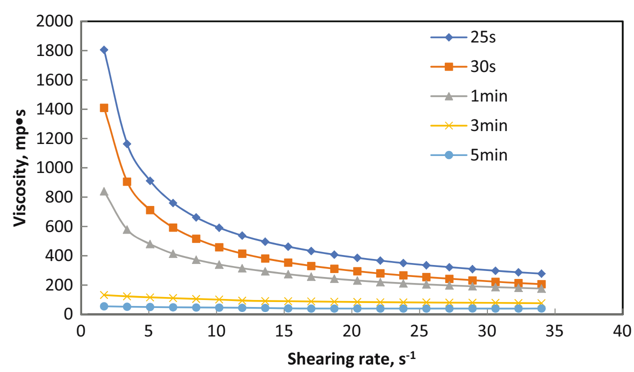

Figure 12: The relationship among the viscosity, shearing rate, and the stirring time (the percentage of the HCl solution (5%) is 0.375%).

than 0.375%, the emulsion system was observed to be in an alkaline medium and the emulsifier formed can stabilize the water-in-oil emulsion.

3.4 Discussion

The deeper understanding of the three stages during the w/o emulsion to o/w emulsion process of the reversible inversion emulsion relies on the result of the studies (Figure 17).

(1) In the first stage, first, what can be seen through the optical microscopy was the closeness degree of the structures among water droplets would first increase and then decrease following the increase of the percentage of the HCl solution (5%) and the most closely structure among water droplets emerged when the percentage of the HCl solution (5%) is 0.2%. The result of the microstructure observation agreed with the result of the viscosity experiment

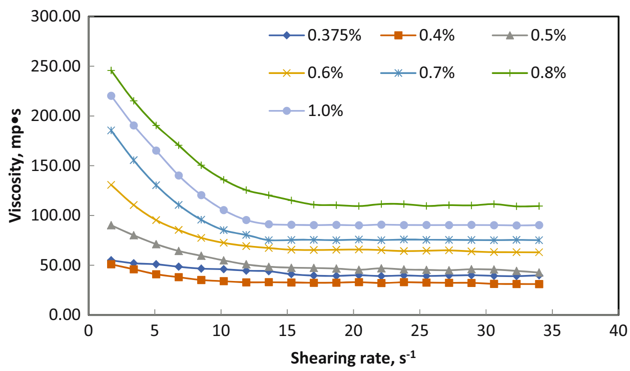

Figure 13: The relationship among the viscosity, the shearing rate, and the percentage of the HCl solution (5%; from 0.375% to 1.0%).

and the changing trend of the volume of the upper oil phase and bottom water phase. Second, the water droplet size would first decrease and then increase following the increase of the percentage of the HCl solution (5%), and the least water droplet size emerged at the point when the percentage of the HCl solution (5%) is 0.2%. The result of the

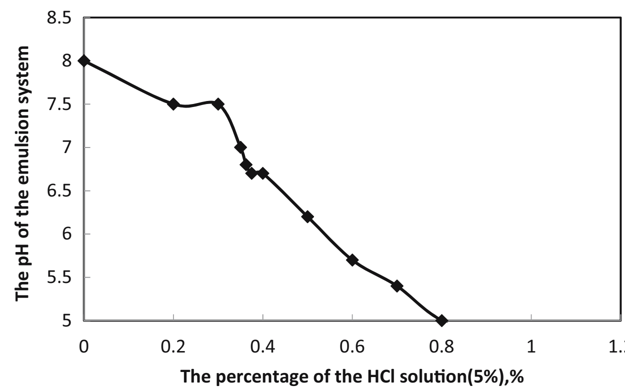

Figure 16: The change in the pH following the change in the percentage of the HCl solution.

microstructure observation agreed with the result of the electrical stability experiment.

(2) In the second stage, the structure among water droplets existed at the beginning of this stage, and the water droplets in the oil phase coalesce into the continuous phase breaking the continuous oil into oil droplets following the increase in the stirring time. The internal phase and the external phase can

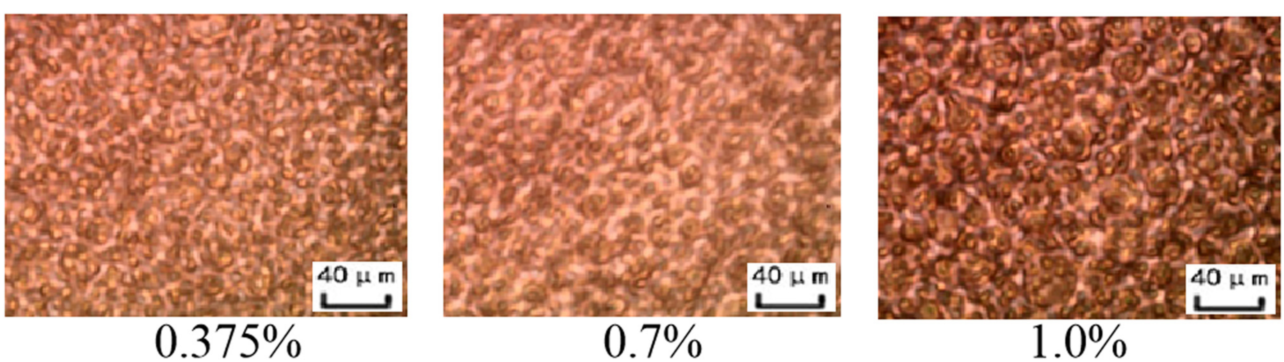

Figure 14: The relationship between the microstructure and the percentage of HCl solution (5%; from 0.375% to 1.0%).

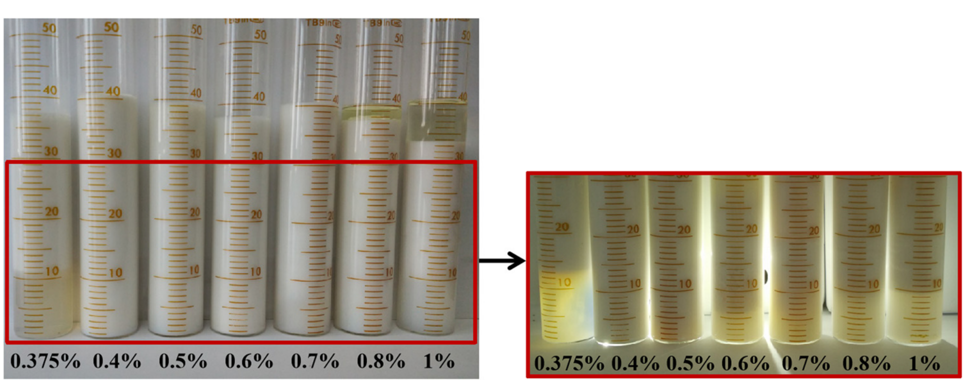

Figure 15: Photograph of emulsions with different percentages of the HCl solution (5%; percentage from 0.375% to 1.0%, and stirring time is 5 min) after 24 h of preparation.

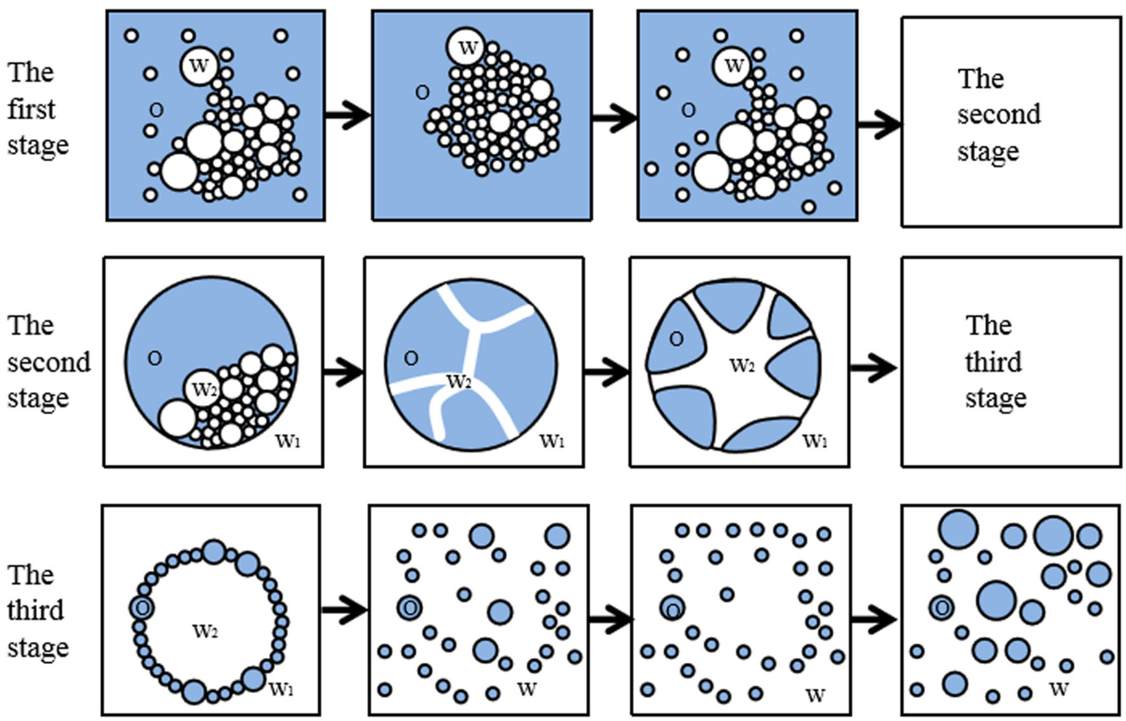

Figure 17: The diagram of three stages during the w/o emulsion to o/w emulsion process of the reversible inversion emulsion.

interchange positions during the process. The w/o/w emulsion would change into o/w emulsion at the end of this stage. The result of the viscosity experiment of the emulsion agrees with the phenomenon that the coalescence of the oil droplet would be easily broken during the standing.

(3) In the third stage, the structure among oil droplets of the emulsion would be broken following the increase in the stirring time (the percentage of the HCl solution (5%) is 0.375%) and the oil droplets dispersion degree in the emulsion would become better. The viscosity of the emulsion system would decrease following the destruction of the structure among water droplets of the emulsion. The results of the microstructure observation agreed with the result of the conductivity experiment and the viscosity experiment. The oil droplet size would first fall down and then rise up following the increase in the percentage of the added HCl solution (5%) (stirring time is 5 min) and the minimum oil droplet size emerged in the point when the percentage of the HCl solution (5%) is 0.4%. In this part, the percentage of the HCl solution (5%) is more than 0.375%. The viscosity of the emulsion also would first decrease and then increase following the changing trend of the volume of the oil droplets of the emulsion and the minimum viscosity also emerged when the percentage of the HCl solution (5%) is 0.4%. The result of the microstructure observation agrees with the result of the viscosity experiment.

4 Conclusion

From the experimental study, the following conclusions were made.

(1) Increasing the percentage of HCl would cause an alteration in the closeness of the structure among the droplets in the system and hence affecting the microstructure of the emulsion.
(2) The percentage of the HCl solution in the system will also affect the viscosity of the emulsion and hence affect the microstructure of the emulsion.
(3) The optimum level of the HCl solution (0.2%) in the emulsion system will give a higher volume of emerged oil, and it can be deduced that the changing trend of the volume of the upper oil affects the microstructure of the emulsion.
(4) The electrical stability of the microstructure is also related to the amount of the acid solution in the emulsion system.
(5) Increasing the stirring time will also increase the stability of the oil droplets in the system as the breakage of the structure among the oil droplets causes more free oil droplets to accumulate in the emulsion.

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