Effects of ice formation/dissociation on the stability of water-in-oil emulsions

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Abstract

In this study, a three cooling-heating cycle procedure was used for determining the effects of ice formation/dissociation on the stability of water-in-oil emulsion using a differential scanning calorimetry (DSC). And the effects of NaCl and Arquad 2HT-75(a model hydrate antiagglomerant) were discussed. Both the DSC test and visual Bottle test suggest that, mass transfer happens during ice formation due to "solidification ripening" mechanism. Therefore, ice formation/dissociation could destabilize water-in-oil emulsion, accelerating the separation of water and oil. Furthermore, the addition of NaCl and Arquad 2HT-75 can help to form stable water-in-oil emulsion, but they cannot prevent ice formation/dissociation from destabilizing water-in-oil emulsion. This study also indicates that although both hydrate and ice formation/dissociation can lead to destabilization of the water-in-oil emulsion, the demulsification mechanisms are different. In addition, DSC can be used as a useful tool to determine emulsion droplet size, investigating the change of droplet size distribution under certain condition.

Keywords

ice formation/dissociation, mass transfer, differential scanning calorimetry, water-in-oil emulsion, solidification ripening

1. Introduction

For the oil-dominated system, due to the turbulence in flow in pipelines, water typically is dispersed into the oil phase, creating a water-in-oil (W/O) emulsion [1]. For the oil and gas flowlines in high latitude areas and ultra-deep water, due to the much lower environment temperature, the free water dispersed in the oil would form ice or hydrate under certain conditions[2]. The formation and accumulation of ice/hydrate in flowlines can lead to flowline blockage, resulting in potential operational failures [2-4]. In fact, not only the appearances of ice and hydrate are similar, but also most of their properties (e.g., mechanical, elastic and thermal properties) are close[2]. Therefore, ice is usually a reference for hydrate research. The previous works found that, hydrate formation can lead to agglomeration of hydrate particles and water droplets, resulting in destabilization of the water-in-oil emulsion[3-5]. However, the effects of ice formation/dissociation on the stability of water-in-oil emulsion are not well understood[5]. In this study, the effects of ice formation/dissociation on the stability of water-in-oil emulsion were investigated using differential scanning calorimetry. And the effects of NaCl and Arquad 2HT-75(a model hydrate antiagglomerant) were discussed.

2. Experimental Methods and Materials

2.1 Apparatus

The majority of experiments were performed in a micro-differential scanning calorimeter (μ-DSC VIIa, Setaram Inc.) The μ-DSC could be used to measure the thermal properties of ice in W/O emulsified system at atmospheric conditions [6]. The thermocouples in the calorimetric furnace measure the temperature difference between the reference and sample cells, and the heat necessary to achieve a zero temperature difference between the cells is recorded [7].

For this work, a Cyclone IQ2 Microprocessor Controlled Homogenizer (VirTis Co.) was used for preparing emulsions[5]. It consisted a control box and a mixing unit that allowed an rpm range from 5000 to 30,000. The homogenizer shaft was a 10mm rotor/stator shaft assembly. A Olympus IX71 microscope (Olympus Co.) was used for observing the morphology of the emulsions. A 1196D refrigeration unit (VWR International, Inc.) was used for visual testing and observing the effects of ice formation/dissociation on the stability of emulsion.

2.2 Materials.

The crude oil used was a low API gravity oil with a viscosity of 100±1.5 cP at 20 ℃ and 100 s-1 and a density of 0.908 ± 0.003 g/cm3[8]. The interfacial tension value for the crude oil-water was measured to be 28.9 ±0.4 mN/m under atmospheric conditions. The oil has a saturated, asphaltene, resin, and aromatic (SARA) content of 49.1 wt.%, 1.7 wt.%, 20.2 wt.%, and 29 wt.%, respectively.

The water phased is deionized water or mimic sea water which including 3.5 wt.% Sodium chloride(NaCl, Macron Chemicals) in the deionized water. The model anti-agglomerant, Arquad 2HT-75 (75% dehydrogenated tallow dimethylammonium chloride in water/isopropyl alcohol, Sigma-Aldrich®, 88-92% purity) was selected[9](Fig. 1).Do not number your paper: All manuscripts must be in English, also the table and figure texts, otherwise we cannot publish your paper. Please keep a second copy of your manuscript in your office. When receiving the paper, we assume that the corresponding authors grant us the copyright to use the paper for the book or journal in question. Should authors use tables or figures from other Publications, they must ask the corresponding publishers to grant them the right to publish this material in their paper. Use italic for emphasizing a word or phrase. Do not use boldface typing or capital letters except for section headings (cf. remarks on section headings, below).

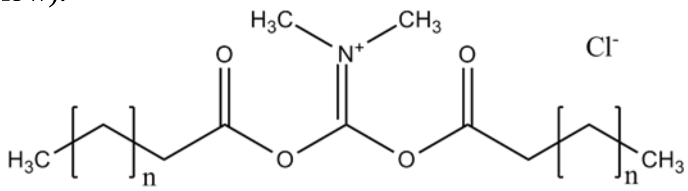

Fig. 1 Structure for Arquad 2HT-75 (n = 12-18)

2.3 Procedures.

Emulsion preparation method

Around 30 mL of oil was measured out in a glass beaker. If Arquad 2HT-75(AA) was being used in the emulsion, then the AA (2 wt. %) was measured and added to the oil, at which point the AA was dissolved in the oil by use of a magnetic stirrer and was subject to low heating (50 ℃) for a proper dissolution of wax and other content in the crude oil. The beaker with the oil was then placed under the homogenizer and the control box was set to mix at 8000 RPM. The mixtures were stirred for 3 min, while water/model seawater was added drop by drop using a plastic syringe during the first minute. After preparation, the emulsions were poured into 100mL glass flask. In all cases, 60 mL emulsion samples are prepared.

Emulsion preparation method

In order to investigate the effects of ice formation/dissociation on the stability of emulsion, the original emulsions should have relatively good initial stability. Due to the DSC tests will last about 1d, the optical microscope was used for observing the morphologies of fresh emulsions and aged emulsions (1d). In addition, Phase separation is monitored daily by classical Bottle test for a period of 6 days. This test was performed at room temperature (~22 ℃).

DSC test

For ambient pressure DSC tests, ~15 mg of an emulsion sample was placed in a vessel. The sample was cooled from 30 to -45 ℃ at a rate of 0.3 ℃/min. The sample was then heated back to 30 ℃ at the same rate and this cycle was repeated three times. Furthermore, in order to assist the DSC test, the emulsion was also immerged into the refrigeration unit to allow ice formation /dissociation. The sample was cooled from 20 to -30 ℃ at a rate of 1 °C/2 min, and then the sample was held at −30 °C for 12 h. Next, the sample was then heated back to 30 ℃ at the same rate.

3. Result and Discussion

3.1 Emulsion stability tests

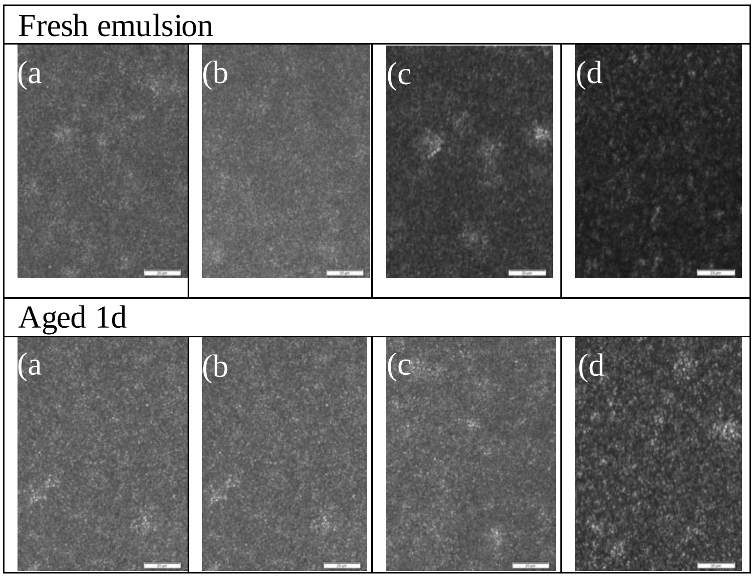

Fig. 2. Micro morphologies of fresh emulsions and aged emulsions with 1d (a) blank, (a) +3.5wt.%salt, (a) +2wt.% AA and (a)+3.5wt.%salt+2wt.% AA.

Fig. 2 shows the morphologies of fresh emulsions and aged emulsions (1 day). For all the emulsions, the morphologies of 0 day(fresh) and 1day were found to show insignificant changes. It suggests that the four emulsions have relatively good initial stability. During the Bottle test, for the blank sample, free water was observed about two days after emulsification. For sample with 2wt.%AA, a small amount of free water was observed at the bottle bottom after 5 days. The two other samples were stable for at least 6 days. The results from the Bottle tests suggest that salt, AA and their combination can help the mixture to form stable water-in-oil emulsion.

3.2 DSC test

Droplet size, as the most important for the characterization of the emulsion, can affect various properties (e.g. stability, rheological properties, optical properties etc.) of emulsion [10,11]. From nucleation theory and experimental study, Dalmazzone et al. and Montengro et al. showed that a lower nucleation temperature is required for a smaller water droplet size in an emulsion system [12,13]. This further suggests that the knowledge of the droplet freezing temperatures is a mean to get information about their sizes and consequently about the way the emulsion evolves with different process. Thus, DSC becomes an a useful tool to determine emulsion droplet size, and shows unique advantages for the concentrated and opaque emulsions, as compared with other commonly used techniques [14].

Fig. 3(a) shows the ambient pressure thermogram for the blank sample. For three cycles, two kinds of unequal-sized exothermal peaks observed upon cooling. The large intensity peaks appeared at -16 ℃ ~-21 ℃ suggests the presence of bulk water or isolated large water droplets [1], while the small intensity peaks, almost invisible by naked eye from the original figure, appear at -38 ℃~-40 ℃, indicates the presence of micro-sized droplets and confirms that the sample is a water-in-oil emulsion [5,15]. In the heating portion of the thermogram, only one endothermic peak near 0 ℃ is observed, corresponding to ice melting. Comparing the intensity of the two types of exothermal peak, it can be concluded that the blank sample is constituted mainly of large water droplets (cycle 1). Furthermore, upon increasing the cycle, more large intensity peaks are observed at higher nucleation temperature and the small intensity peak become smaller. Both changes suggest that ice formation and melting destabilize the emulsion. The reason can be explained in term of the “solidification ripening” mechanism. As aforementioned before, freezing is the result of nucleation phenomena and consequently all the droplets do not freeze at the equilibrium point. And the different droplet sizes will induce their freezing temperatures are scattered. Therefore, it can happen that some droplets are already frozen and others are not. In such a situation, a matter transfer can occur from the still undercooled droplets to the already frozen ones [14]. This matter transfer is expected to induce a change in drop size distribution (e.g., small droplet amount becomes less and larger droplets arise).

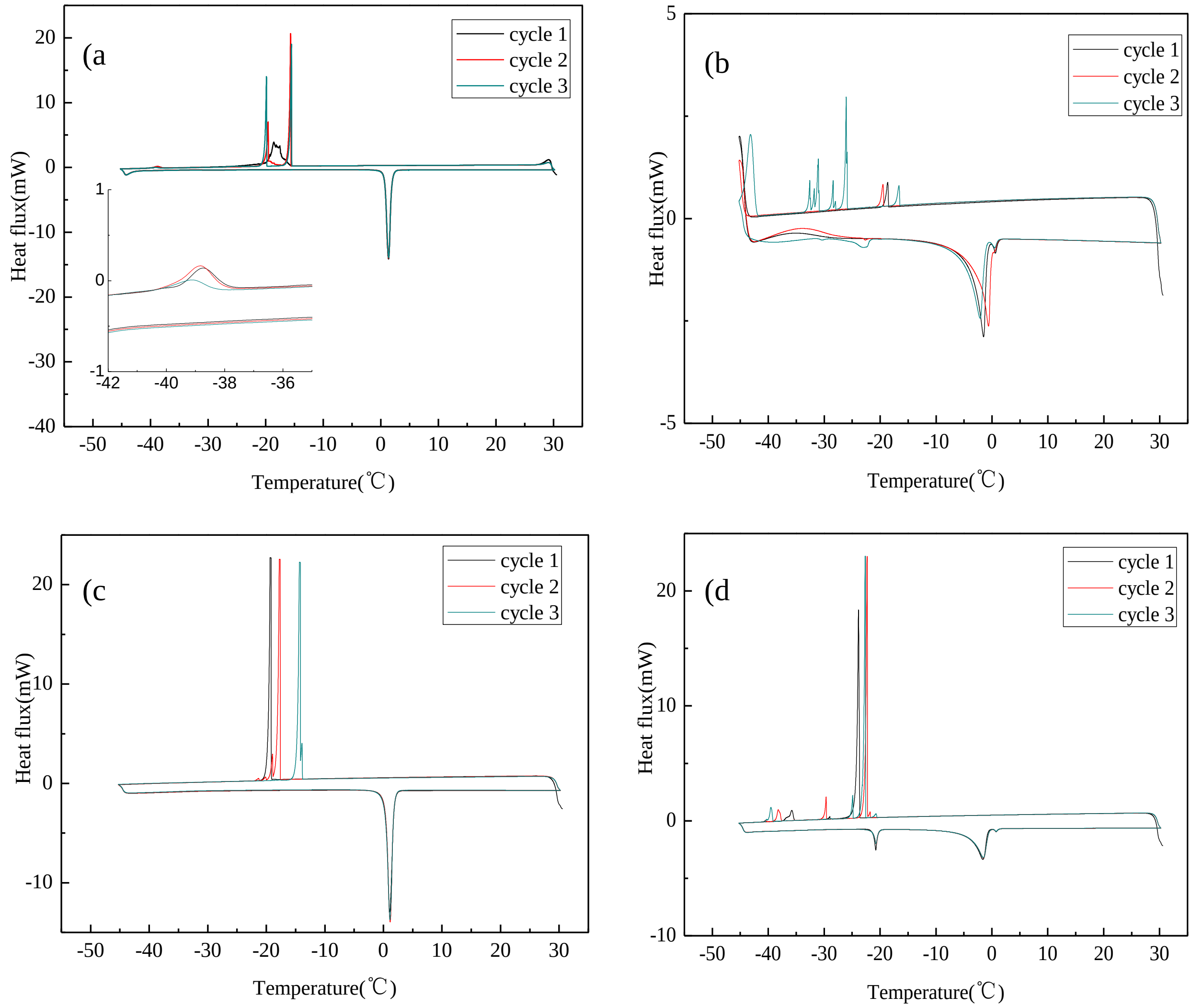

Figure 3. Ambient pressure thermograms for emulsions with (a) blank (b) 3.5wt.%salt (c) 2wt.%AA and (d) 3.5 wt.%salt +2wt.%AA.

Fig. 3(b) presents the ambient pressure thermogram for the 5 emulsion with 3.5wt.% salt. For cycle 1 and 2, during the cooling portion of the thermogram, one small intensity peak appeared at -20 ℃, and another large peak begins to appear at -45 ℃ and extends to the heating portion. Comparing the intensity of the two exothermal peaks, it suggests that the water droplets are well dispersed and constituted mainly of micro-sized droplets. During heating, only one endothermic peak near -2 ℃ is observed due to the progressive melting of ice. And the difference of ice melting temperature compare with the blank sample is owing to the presence of the salt. For cycle 3, in addition to the peaks appeared at -20 ℃ shift to higher nucleation temperature, multi-exothermal peaks also emerge in the range of -26 ℃ ~-33 ℃ upon cooling. It indicates that mass transfer occurring upon ice formation/dissociation, while in the heating portion, two peaks were observed, one small intensity peak appeared at -22 ℃ and it is immediately followed by a large endothermic peak which is similar to that in cycle 1 and 2. The small intensity peak should correspond to eutectic melting [12]. During the cooling portion, the brine droplets will nucleate at the surface (see Fig. 4(b)). With the nuclation spans the surface, a thin film wraps the droplet and thicking, leading to the salt concentration in the residual water become richer. When the salt concentration in the shrunken droplets reaches about 23.3%, with further decrease of temparature, the salt and water will crystallize at the same time and form eutectic(see Fig. 4(c) and (d)). Therefore, for each particle, the out layer is ice and the core is eutectic. During the heating portion, due to the dissociation temperature of eutectic is -21.4 ℃ and much lower than that of ice, so the melting of particle will from inside to outside and the first endothermic peak should correspond to the dissociation of the eutectic core and the dissociation temperature -22 ℃ of the small endothermic peak in the thermograms confirms this. The reason that the eutectic melting peak does not appeare in cycle 1 and 2 can be explained that, as aforementioned in the cooling portion, there are much more smaller droplets in cycle 1 and 2 and the water phase can't not fully converte into ice during the cooling temperature range in this study, so the salt concentation in the residual water may not reach to the required concentration(23.3%) and consequently no eutectic points are observed, while in cycle 3, bigger droplets formed and that led to higher conversion of ice, and consequently leading to a higher salt concentration in the residual water thus to form eutectic subquently.

With respect to the other thermograms in Fig. 3, the ambient pressure thermogram of emulsion with 2wt.%AA is simpler. As shown in Fig. 3(c), during the cooling portion for the three cycles, there is only one narrow intensity peak appeared between -20 ℃ ~-14 ℃, and the peak shifts to higher nucleation temperature with the passage of subsequent cycles. It suggests that this emulsion is constituted of uniform large water droplets and mass transfer occurred during ice formation/dissociation. During the heating portion, only one intensity peak observed at 0 ℃ due to the melting of ice.

Similar to the blank sample, for the emulsion with combination of salt and AA, two kinds of unequal-sized exothermal peaks were also observed upon cooling. And the more intensity peaks appeared at higher nucleation temperature (-22 ℃~-25 ℃) indicates that this emulsion constituted mainly of larger droplets. Furthermore, mass transfer can also be determined by the change of the peaks. While for the heating portion, eutectic and the progressive ice melting were observed for the three cycles, which is different from that of emulsion with 3.5wt.% salt. This can be explained by the previously established hypothesis [12, 13] that larger drops emerging in this sample, would nucleate at much higher temperatures, and consequently a higher ice conversion would lead to the eutectic formation due to a higher salt concentration.

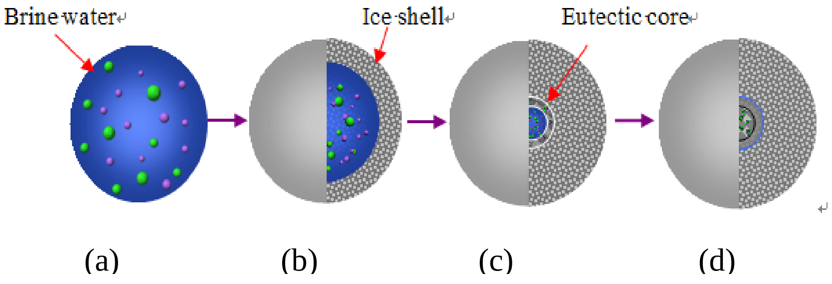

Fig. 4. Concept picture of ice formation from brine droplet

Corresponding to Fig. 3, the visual Bottle test results are showed in Fig. 5. For sample (a)(c)and (d), after ice formation, the emulsions have significant change on appearance, and free water was observed after ice melting. For emulsion (b), no significant change was observed after ice formation and melting. In fact, this is also agreement with the DSC test. As aforementioned before, the emulsion has very fine droplets and the nucleation temperature is very low. At the temperature of -30 ℃, ice conversion is expected to be very low, resulting in the insignificant effect on emulsion stability.

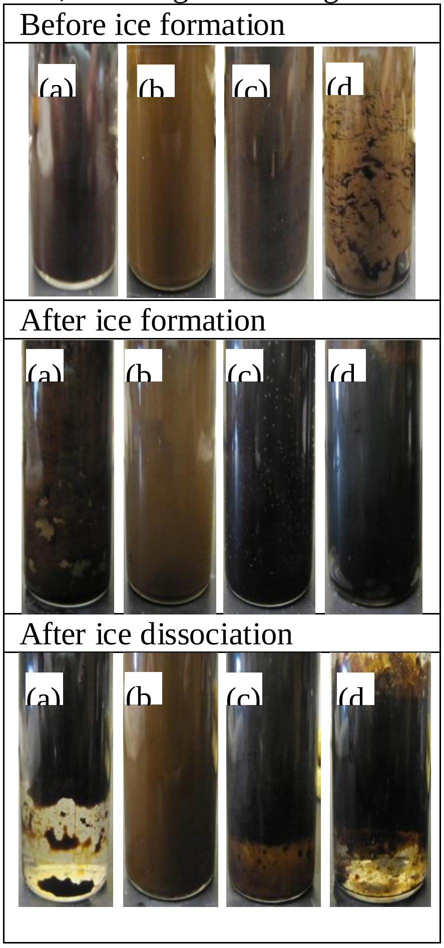

Fig 5. Visual bottle tests of water-in-oil emulsions for 50 vol.% water content. (a) blank (b) 3.5wt.%salt (c) 2wt.%AA and (d) 3.5 wt.%salt +2wt.%AA

In sample (c) and (d), Arquad 2H-75 was added. Arquad 2H-75, as a model hydrate anti-agglomerant, was proved to can prevent hydrate agglomeration under certain conditions [3,16]. However, herein, the addition of Arquad 2H-75 cannot prevent ice formation/melting from destabilizing the W/O emulsion effectively. The difference might be explained by the different demulsification mechanism of hydrate and ice formation/dissociation. During hydrate formation, liquid bridge will form between hydrate particles, resulting in hydrate agglomeration. With the addition of Arquad 2H-75, Arqurd2HT-75 can significantly increase the contact angle of unconverted water on hydrate and thus greatly reduce the ability of water to wet the hydrate particle, essentially preventing liquid bridges from connecting the particles. This could prevent strong co-/adhesion between hydrate particles and the formation of hydrate aggregates. For ice formation, as aforementioned before, the demulsification mechanism is more like due to “solidification ripening”, resulting in mass transfer during ice formation.

4. Conclusions

Both the DSC test and visual Bottle test suggest that, mass transfer happens during ice formation due to “solidification ripening” mechanism. Therefore, ice formation/dissociation could destabilize water-in-oil emulsion, accelerating the separation of water and oil. Furthermore, the addition of NaCl and Arquad 2HT-75 can help to form stable water-in-oil emulsion, but they cannot prevent ice formation/dissociation from destabilizing water-in-oil emulsion.

References

[1] Delgado-Linares, J. G., Majid, A.A., Sloan, E.D., Koh, C.A., Sum, A.K. Model Water-in-Oil Emulsions for Gas Hydrate Studies in Oil Continuous Systems. Energy & Fuels, 2013, 27, 4564-4573.

[2] Sloan, E. D., & Koh, C. A. Clathrate Hydrates of Natural Gases. 3rd Ed., CRC Press-Taylor & Francis Group, Boca Raton, FL. 2008.

[3] Liu, C.W., Li, M.Z., Srivastava, V.K., Koh, C.A. Investigating Gas Hydrate Formation in Moderate to High Water Cut Crude Oil Containing Arquad and Salt, Using Differential Scanning Calorimetry. Energy & Fuels, 2016, DOI: 10.1021/acs.energyfuels.5b02433.

[4] Liu, C. W., Li, M. Z., Zhang, G. D., Koh, C. A. Direct measurements of the interactions between clathrate hydrate particles and water droplets [J]. Phys. Chem. Chem. Phys., 2015, 17, 20021-20029.

[5] Lachance, J. W., Sloan, E. D., Koh, C. A. Effect of hydrate formation/dissociation on emulsion stability using DSC and visual techniques. Chem. Eng. Sci. 2008, 63, 3942 −3947.

[6] Setaram. Micro DSC VII Commissioning Utilisations, 2003.

[7] Sorai, M. Comprehensive Handbook of Calorimetry and ThermalAnalysis, Maruzen Company Limited, 1998.

[8] Sjoblom, J., Øvrevoll, B., Jentoft, G. H., Lesaint, C., Palermo,T., Sinquin, A., Gateau, P., Barre, L., Subramanian, S., Boxall, J.,´Davies, S., Dieker, L., Greaves, D., Lachance, J., Rensing, P., Miller, K.,Sloan, E. D., Koh, C. A. Investigation of the Hydrate Plugging and Non-Plugging Properties of Oils. J. Dispersion Sci. Technol. 2010, 31, 1100 −1119.

[9] Thompson, D. G., Taylor, A. S., Graham, D. E. Emulsification and Demulsification Related to Crude Oil Production. Colloids Surf. 1985, 15, 175 −189.

[10] Liu, C. W., Li, M. Z., Liang, C., et al. Measurement and analysis of bimodal drop size distribution in a rotor-stator homogenizer[J]. Chemical Engineering Science. 2013, 102, 622-631.

[11] Liu, C. W., Li, M. Z., Han, R., et al. Rheology of Water-In-Oil Emulsions with Different Drop Sizes[J]. Journal of Dispersion Science and Technology, 2016, 37, 333–344.

[12] Dalmazzone, C., Noïk, C., Clausse, D. Application of DSC for Emulsified System Characterization. Oil Gas Sci. Technol. 2009, 64, 543−555.

[13] Montenegro, R., Antonietti, M., Mastai, Y., Landfester, K. Crystallization in Miniemulsion Droplets. J. Phys. Chem. B. 2003, 107, 5088 −5094.

[14] Clausse, D., Gomez, F., Pezron, I., Komunjer, L., Dalmazzone, C. Morphology characterization of emulsions by differential scanning calorimetry. Adv. Colloid Interface Sci. 2005, 117, 59 −74.

[15] Santini, E., Liggieri, L., Sacca, L., Clausse, D., Ravera, F. Interfacial rheology of Span 80 adsorbed layers at paraffin oil–water interface and correlation with the corresponding emulsion properties. Colloids Surf., A. 2007,309, 270-279.

[16] McCulfor, J., Himes, P., Anklam, M. K. The effects of capillary forces on the flow properties of glass particle suspensions in mineral oil. AIChE J. 2011, 57, 2334−2340.