



Emulsion stability of surfactant and solid stabilized water-in-oil emulsions after hydrate formation and dissociation

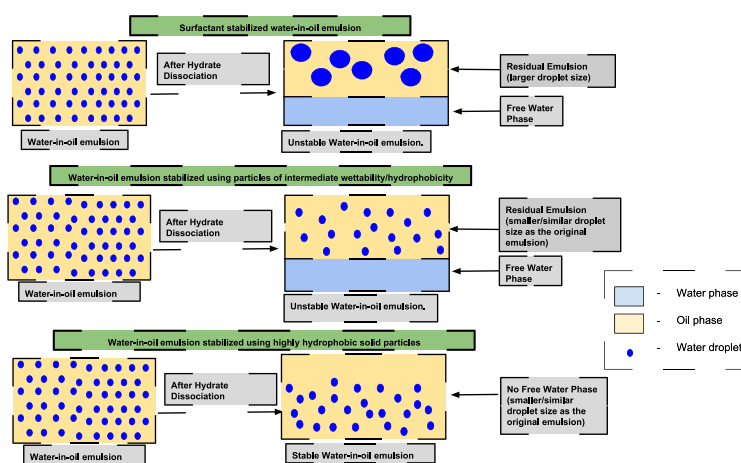
Ashwin Kumar Yegya Raman, Deepika Venkataramani, Swanand Bhagwat, Tyler Martin, Peter E. Clark, Clint P. Aichele*

School of Chemical Engineering, Oklahoma State University, Stillwater, OK 74078, United States

HIGHLIGHTS

- The effect of hydrate formation/dissociation on W/O emulsions stabilized using solid particles of varying hydrophobicity was investigated.
- W/O emulsions stabilized with highly hydrophobic particles resisted destabilization due to hydrate formation/dissociation.
- W/O emulsions stabilized using surfactant or partly hydrophobic particles exhibited destabilization due to hydrate formation/dissociation.
- Residual droplet size of surfactant stabilized emulsions increased after hydrate formation/dissociation unlike solid stabilized emulsions.
- Presence of solid particles at the liquid-liquid interface did not modify the IFT value significantly unlike surfactants.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydrates are ice-like crystalline compounds that can cause plugging of crude oil pipelines. Stable water-in-oil emulsions aid in preventing hydrate particle agglomeration and hydrate plug formation in crude oil pipelines. The type of stabilizers present in water-in-crude oil emulsions also influences hydrate formation. Therefore, the effect of hydrate formation and dissociation on the stability of water-in-oil emulsions stabilized using either surfactants or solid particles was investigated. In addition, the difference in the effect of hydrate formation and dissociation on water-in-oil emulsions stabilized using solid particles of varying hydrophobicity was investigated. Furthermore, the effect of hydrate formation and dissociation on droplet size of the water-in-oil emulsions was quantified. The results showed that, the water-in-oil emulsions stabilized using highly hydrophobic solid particles resisted emulsion destabilization, after hydrate formation and dissociation, unlike water-in-oil emulsions that were stabilized using either surfactants or partly hydrophobic solid particles. Also, after hydrate dissociation, for surfactant stabilized emulsions, the droplet size of water in the residual emulsion increased by more than 85% as compared to the droplet size before hydrate formation. On the contrary, for solid stabilized emulsions, no significant change in the droplet size of the residual emulsion was observed after hydrate dissociation as compared to the water-in-oil emulsion before hydrate formation. A conceptual mechanism was proposed to explain the observed difference in the stability of solid stabilized water-in-oil emulsions when subjected to hydrate formation and dissociation. Additionally, dynamic interfacial tension measurements were carried out to explain the difference in the initial droplet size of solid stabilized and surfactant stabilized water-in-oil emulsions.

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1. Introduction

Emulsions are in general colloidal dispersions of a liquid in another immiscible liquid stabilized using surfactant and/or solid particles. Emulsions have a wide variety of industrial applications such as those in energy, cosmetics, pharmaceuticals, and agriculture. In the energy industry, emulsions are ubiquitously encountered in nearly every stage of production, transportation, and operation [1]. Naturally occurring surfactants such as clay, silica, and inorganic particles present in crude oil systems have been shown to affect the hydrate formation and its characteristics resulting into the flow assurance issues [2–4]. Gas hydrates (also known as clathrates/clathrate hydrates) are non-stoichiometric, ice-like crystalline structures formed from host water molecules and low molecular weight guest gas molecules such as methane, ethane, and propane at low temperatures and at high pressures prevalent in subsea conditions [5]. Hydrate formation is one of the most important flow assurance problems since hydrate formation occurs more rapidly as compared to formation of wax and asphaltenes. Furthermore, huge amount of money is spent in managing and mitigating pipeline blockages due to hydrate formation [5]. Hydrate formation may occur during operations such as start-up, restart, shut in, and in places in the pipeline where there is a change in flow geometry, across valves, risers, and offshore/subsea systems [6].

Hydrates are classified as either structure I, II, or H depending on the cage size and guest gas molecule [7]. Structure I hydrates are composed of twelve pentagonal (5^{12}) and two hexagonal (6^2) cavities occupied by guest molecules such as methane, ethane, and carbon-dioxide [7]. Structure II hydrates are the most common type in the oil and gas industry, and are composed of $5^{12}6^4$ cavities and occupied by guest molecules such as propane and *iso*-butane. Structure H hydrates are composed of high molecular gas compounds and are the least common type [7]. This paper focuses on the investigation of structure II hydrates. Although, hydrates are generally formed at high pressure and low temperature conditions, cyclopentane hydrates and tetrahydrofuran (THF) hydrates are formed at atmospheric conditions. Tetrahydrofuran is miscible with water and hence does not provide mass transfer limitations that is generally observed with natural gas hydrates. Hence, tetrahydrofuran was not used as the hydrate forming guest molecule. Cyclopentane is a useful guest molecule to investigate structure II hydrates since cyclopentane forms structure II hydrates, which is similar to natural gas hydrates. In addition cyclopentane hydrates can be formed at atmospheric pressures and at a temperature of around 7 °C [8]. Thus, cyclopentane was used as the hydrate forming guest molecule.

Hydrate management is economically feasible and favorable when compared to complete avoidance due to excessive capital and operating costs involved in completely preventing hydrate formation [9]. Formation of water-in-oil emulsions (water dispersed in continuous oil phase) is one of the most predominant multiphase flow situation encountered in petroleum industry. The key objective of this manuscript is to investigate the influence of hydrate formation and dissociation on water-in-oil emulsions. Lachance et al. [10] studied the effect of hydrate formation and dissociation on the stability of water-in-crude oil emulsions. They concluded that hydrate formation and dissociation led to destabilization of emulsions. Hydrate formation is generally dependent on the crude oil properties. Crude oil contains various natural surfactants such as asphaltenes, resins and carboxylic acids. Furthermore, the type of surfactant and the concentration of surfactant in crude oil affects

hydrate formation [11,12]. Raman et al. [13] studied the effect of stabilizers on hydrate formation and their rheological behavior in hydrate forming water-in-oil emulsions. They concluded that the solid particles promote hydrate formation to a greater extent as compared surfactants. Thus, the type of stabilizer affects hydrate formation.

For effective hydrate management strategies in water-in-oil emulsions, the amount of water present in the emulsion plays a crucial role [14]. Finely dispersed water-in-oil emulsions help in mitigating the hydrate blockages [6]. Thus, droplet size of water-in-oil emulsion plays an important role in hydrate management strategies. In addition, droplet size affects the rheological properties of water-in-oil emulsions. Furthermore, the stability of emulsion influences the flow friction factor [15–18]. Unstable emulsions leads to a drag-reduction behavior unlike surfactant-stabilized emulsions. Thus, investigating the effect of hydrate formation and dissociation on emulsion stability and on the droplet size of water-in-oil emulsions would provide a better insight on the flow behavior of water-in-oil emulsions before hydrate formation and after hydrate dissociation.

Hydrate formation is an interfacial phenomenon that takes place when hydrocarbons dissolved in the oil phase come in contact with the water phase [6]. Thus, interfacial characterization of oil-water interface in the presence of various stabilizers becomes critical.

The objective of this paper was to investigate and compare the effect of hydrate formation and dissociation on water-in-oil emulsions stabilized using either surfactants or solid particles. Different types of stabilizers were used to investigate the effect of hydrophobicity of solid particles on the stability of water-in-oil emulsions upon hydrate formation and dissociation. In addition, our objective was to quantify the effect of hydrate formation and dissociation on droplet size of the water-in-oil emulsions stabilized using either surfactants or solid particles. Furthermore, interfacial tension measurements were carried out to elucidate the effect of stabilizers on the interfacial properties of water-in-oil emulsions.

2. Materials and methods

2.1. Materials used

Water-in-oil emulsions were investigated in order to gain insight on the effect of hydrate formation and dissociation on emulsion stability. Deionized water with a resistivity of 18.2 mΩ cm⁻¹ was used to form the internal phase. The continuous oil phase consisted of light mineral oil (+99% purity, sigma Aldrich), and either cyclopentane (+95% purity, Alfa Aesar) or *iso*-octane (+99.48%, Honeywell). Cyclopentane was used as the hydrate-forming component. Sorbitan monooleate (Span 80), an oil soluble, non-ionic surfactant was used to stabilize the water-in-oil emulsions. The HLB [19] value of Span 80 is 4.3 ± 1.0 (as stated by the vendor). Span 80, though, a smaller molecule as compared to asphaltenes, can resemble the surface activity of asphaltenes [10]. Hence, for investigation of surfactant stabilized water-in-oil emulsions, Span 80 was used as the surfactant. For preparation of solid stabilized water-in-oil emulsions, two types of solid particles with different hydrophobicity were chosen. Solid stabilized water-in-oil emulsions were either stabilized using Aerosil R974 (highly hydrophobic solid nanoparticle, provided by Evonik Inc.) or Aerosil R104 (partly hydrophobic solid nanoparticle, provided by Evonik Inc.).

Water-in-oil emulsions were investigated at two different water cuts viz. at 20 vol.% and 40 vol.% water cut. The concentration of the emulsifiers (Span 80, Aerosil R974 and Aerosil R104) were kept constant at 0.1 vol.% (based on total volume) for all water fractions. The critical micelle concentration (CMC) of Span 80 is 0.03(%v/v) [20,21]. Thus, under the current study, for the water-in-oil emul-

* Corresponding author.

E-mail address: clint.aichele@okstate.edu (C.P. Aichele).

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