Fuel 179 (2016) 141–149

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

# A comparison of the rheological behavior of hydrate forming emulsions stabilized using either solid particles or a surfactant

Ashwin Kumar Yegya Raman, Samyukta Koteeswaran, Deepika Venkataramani, Peter Clark, Swanand Bhagwat, Clint P. Aichele *

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

ARTICLE INFO

*Article history:*
Received 4 November 2015
Received in revised form 13 March 2016
Accepted 14 March 2016
Available online 21 March 2016

*Keywords:*
Clathrate hydrates
Rheology
Flow assurance
Emulsions

ABSTRACT

Simple clathrate hydrates are non-stoichiometric, ice-like crystalline compounds that can, among other things, cause blockages of oil and gas pipelines. More challenging exploration and development has emphasized the need to investigate the rheological behavior of hydrates in order to ensure continuous production of crude oil through pipelines especially for solid stabilized emulsions. Therefore, a difference in the rheological behavior of hydrate forming water-in-oil emulsions stabilized using either solid particles (Aerosil R974, fumed silica particles) or a surfactant (Span 80, a non-ionic surfactant) over a range of water cuts is investigated. A rheometer with helical ribbon geometry was used to investigate the rheological behavior of hydrate slurries as opposed to conventional standard geometries. Cyclopentane was used as the hydrate-forming component. The results showed that hydrate formation was rapid in the presence of solid particles compared to surfactant. We hypothesize that solid particles act as nucleation sites and reduce the induction time required for hydrate formation. In addition, the viscosity of water-in-oil emulsions increased with an increase in water cut. Hydrate forming emulsions formed using solid particles had a higher viscosity than emulsions formed using surfactant.



## 1. Introduction

Flow assurance problems are a major concern to offshore energy development [1]. Some of the flow assurance problems include formation of hydrates, waxes, asphaltenes, and corrosion of pipelines. Of all the flow assurance problems, hydrate formation is the most critical to address [2] because hydrate formation takes place within hours unlike waxes or asphaltenes that takes weeks or months to form. Simple clathrate hydrates are ice-like crystalline solid compounds that consists of hydrogen bonded water molecules [3]. Hydrates consists of two components – host and guest molecules. In simple clathrate hydrates, the host molecule is water, whereas, the guest molecules are low molecular weight hydrocarbons such as methane, ethane, propane, and also gases such as carbon-di-oxide, nitrogen, oxygen, and hydrogen sulfide. They are formed when guest molecules are completely enclosed inside the host molecules at suitable conditions. Based on the cage size and guest molecule, simple clathrate hydrates are classified into three predominant structures namely structure I, structure II, and structure H [3]. The cubic structure I, consists of 46 water molecules, arranged in such a way that two pentagonal dodecahedron ($5^{12}$) and six tetrakaidecahedra ($5^{12}6^2$) are formed [3,4]. The cubic structure II, predominantly man-made, consists of 136 water molecules, arranged in such a way that sixteen pentagonal dodecahedron ($5^{12}$) and eight hexakaidecahedron ($5^{12}6^4$) are formed [3,4]. Structure H hydrates, which consists of 34 water molecules, is formed by both large and small guest molecules [3].

Hydrate formation, in an oil-dominated system (higher oil content), is an interfacial phenomenon that takes place when gas/hydrocarbon (guest) molecules that are dissolved in the oil phase come in contact with the water phase (host molecules) under suitable conditions. Hydrates are generally formed at high pressure and low temperatures [3]. However, cyclopentane and tetrahydrofuran (THF) hydrates are formed at atmospheric pressure. Although, THF hydrates are formed at atmospheric pressures, THF is miscible with water that restricts the mass transfer limitation that is found to occur in gas hydrate forming emulsions in crude oil pipelines. Cyclopentane is a useful guest molecule for studying hydrates since both cyclopentane and natural gases form structure II hydrates. Cyclopentane hydrates have a dissociation temperature of 7 °C [5]. Hence, in this study cyclopentane is used as the guest molecule to form hydrates.

* Corresponding author at: School of Chemical Engineering, Oklahoma State University, Stillwater, OK 74078, United States. Tel.: +1 405 744 9110.
*E-mail address:* clint.aichele@okstate.edu (C.P. Aichele).

http://dx.doi.org/10.1016/j.fuel.2016.03.049
0016-2361/

Exploration of oil at more challenging conditions has emphasized the need to study hydrate formation in water-in-oil emulsions. Hydrate formation depends on crude oil properties. Crude oils have natural surfactants such as asphaltenes, resins, carboxylic acids that aid in formation of stable emulsions [6,7]. These natural surfactants that adsorb on to the oil–water interface have both polar and non-polar ends that stabilize water droplets in crude oil. Also, twin-tailed or bulk tail surfactants are present in the crude oil to stabilize the water droplets. Thus, formation of water-in-oil emulsions becomes inevitable in crude oil production. Surfactants play an important role in formation of emulsions. Although, thermodynamics of hydrate formation is well understood, kinetics of hydrate formation is not yet fully understood. The concentration and type of surfactant influence hydrate formation [8,9]. Hence, type of emulsion stabilizers used plays an important role in the process of hydrate formation.

Hydrate formation in crude oil pipelines leads to a decrease in effective flow path of crude oil and thereby leads to an increase in the pressure drop along the pipe. Also, during hydrate formation, the capillary forces between hydrate particles cause binding of water droplets leading to agglomeration that in turn increases the flow resistance. Hydrate formation generally causes an increase in pressure drop and can lead to blockage of the flow line. The phase transformation that takes place due to hydrate formation can alter the flow properties of a mixture that in turn affects the rheological behavior of the mixture. Viscosity of the mixture is essential in determining the pressure drop. Hence, knowledge of rheological behavior of hydrate systems will help in enhancing the design of multiphase pipelines.

Hydrate management measures are typically more economically feasible than hydrate avoidance measures [2]. Also, hydrate remediation measures such as depressurization, thermal, and electrical heating methods become difficult to implement in subsea pipelines. Also, depressurization involves multiple safety concerns. Consequently, knowledge of rheological behavior of hydrates and the influence of surfactants and solid particles on flow properties becomes important for efficient hydrate management measures.

Karanjkar [10] studied the rheology of water-in-oil emulsions formed using Span 80 surfactant over varying water cuts. To extend this work, we focused on solid stabilized emulsions. Recent work by Ahuja [11,12] showed the dependence of hydrate formation and rheology on particles concentration by adding solid particles to water-in-cyclopentane emulsions stabilized using Span 80. The objective of our work was to compare the rheological behavior of hydrate forming water-in-oil emulsions that are formed using either solid particles or a surfactant over a range of water fractions. In addition, a non-standard rheometer geometry (i.e., helical geometry) was used to characterize the rheology of hydrate forming water-in-oil emulsions as opposed to standard rheometer geometries.

## 2. Materials

The emulsions used in this study were formed using deionized water (resistivity of 17.3 m$\Omega$ cm$^{-1}$), light mineral oil (+99% purity, Sigma Aldrich) and cyclopentane and iso-octane (+99% purity, Sigma Aldrich). The model oil emulsions were stabilized using Span 80 (Sorbitan Monooleate) and a hydrophobic silica nanoparticle (Aerosil R974, provided by Evonik). Span 80 is an oil soluble, non-ionic surfactant with an HLB value [13] of 4.3 ± 1.0 (as stated by vendor). Lachance et al. [14] have successfully used Span 80 molecules that are smaller than asphaltene molecules to resemble the surface activity of asphaltenes in crude oil. Hence, Span 80 was used as the surfactant in this study. Aerosil R974 is a hydrophobic fumed silica. The physical properties of the components are given in Table 1. All materials used in this study were used without further purification.

This paper focuses on the rheology of oil continuous emulsions formed using either a surfactant or solid particles. The water cuts were varied from 10 vol.% to 40 vol.%. The Span 80/Aerosil R974 concentration was fixed at 0.1 vol.% based on the total volume. The critical micelle concentration (CMC) of Span 80 is 0.03 (%v/v) [15,16]. Thus, the concentration of Span 80 was well above the CMC value. The oil phase was a mixture of light mineral oil and cyclopentane/iso-octane (50:50 by volume). The amount of cyclopentane was in excess of the stoichiometric requirement for formation of cyclopentane hydrates, which is one mole of cyclopentane to 17 moles of water. In this paper, hydrate forming water-in-oil emulsions refers to emulsions that contain light mineral oil and cyclopentane in the oil phase. The control system refers to water-in-oil emulsions in which the oil phase consists of light mineral oil and iso-octane. Cyclopentane was used as the hydrate-forming component.

### 2.1. Preparation of emulsions

All emulsions were prepared using an IKA T25 digital Ultra-Turrax homogenizer operating at 20,000 rpm for 20 min. The dispenser had a rotor diameter of 17 mm and a stator diameter of 25 mm. First, the cyclopentane/iso-octane was added to light mineral oil followed by the addition of the surfactant/solid particles. Then, the mixture was vigorously shaken so that the surfactant/solid particles was well mixed with the oil phase. In order to achieve homogeneous distribution of the droplet phase, water was added in a drop wise manner to the oil phase [17]. The droplet diameters for all systems investigated were less than 20 μm due to high mixing speed. The control system consists of 40 vol.% water, 0.1 vol.% Aerosil R974, 29.95 vol.% light mineral oil and 29.95 vol.% iso-octane.

### 2.2. Emulsion characterization

Prior to investigating the rheology of hydrate forming water-in-oil emulsions, it must be ensured that the emulsions were stable during the phase of experiment in order to predict the rheological behavior. In order to ensure that the emulsions did not undergo a significant structural change, microscopic investigations were carried out.

The emulsions were characterized using an Olympus BX53 polarized optical microscope equipped with a Linkam temperature controlled shear stage and a high-speed camera. It is well equipped to characterize concentrated water-in-oil emulsions. The mean droplet size of the water-in-oil emulsions was observed immediately after preparation of the sample and after 12 h. Images obtained from the microscope were analyzed using the ImageJ software. Fig. 1 shows micrographs at the 0th hour and after 12 h for 30 vol.% water-in-oil emulsion stabilized using 0.1 vol.% Aerosil R974. Figs. 2 and 3 show the mean droplet size for water-in-oil emulsions stabilized using 0.1 vol.% Span 80 and 0.1 vol.% Aerosil R974 respectively at the 0th hour and after 12 h. A statistical

**Table 1**
Physical properties of components at 25 °C.

| Components | Density (g/ml) | Viscosity (cP) |
|---|---|---|
| Cyclopentane | 0.75 | 0.413 |
| Light mineral oil | 0.838 | >20.5 (at 40 °C) |
| Span 80 | 0.986 | 1200–2000 |
| Aerosil R974 | 2.65 | – |
| Iso-octane | 0.69 | 0.5 |