



Yield stress measurements of cyclopentane hydrate slurry



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ABSTRACT

A hydrate slurry is prepared under shear using liquid cyclopentane (CP) as the hydrate former at atmospheric conditions from a density-matched water-in-oil emulsion, by quenching it to a lower temperature at a fixed shear rate. The typical average drop size is 10 μm . A transition, from initial deformable water drops dispersed in a continuous oil to a solid particle suspension, takes place during which the viscosity increases by several orders of magnitude and jamming may occur. Hydrate slurries so obtained are used for further rheological measurements. In particular, yield stresses are examined for varying water volume fraction using a stress-controlled rheometer. Yield stresses ranged from about 5–4600 Pa between 16% and 30% water volume fraction, with 16% being the minimum water fraction for which there is any measurable yield stress. The yield stress and the final slurry viscosity both scale with water volume fraction as τ_y and $\eta_f \sim (\phi - \phi_c)^{2.5}$, where $\phi_c = 0.15$ as no yield stress is observed for $\phi < 15\%$. Yield stress measurements of CP hydrate slurries allowed to rest after formation under no shearing for a duration are also carried out. Hydrate slurries were found to exhibit shear thinning and significant thixotropic behavior. Direct visualization of hydrate formation on water drops in water-in-oil emulsions is presented.

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1. Introduction

For maximum productivity, it is important to maintain a steady and uninterrupted flow of petroleum in pipelines. Flow blockage in oil and gas pipelines due to solid build-up, which can be due to paraffin, scale, or hydrate formation, is a major challenge in petroleum production. The blockage due to hydrate formation not only leads to large pressure drops in the pipelines but can also lead to emergency shutdown as hydrate growth is a rapid process following a stochastic onset of formation. Clathrate hydrates, also called gas hydrates or simply hydrates, are non-stoichiometric crystals composed of water molecules (hosts) and a gas or liquid molecule (guest). Water molecules may hydrogen bond to form a cage suitable for a guest molecule. The structure becomes stable when a guest molecule is trapped in the cage and interacts with the water molecules through weak van der Waals forces [1,2].

Hydrate slurries exhibit complex rheological behavior [3,4]. This is presumably due to the prevailing three-dimensional microstructure and heterogeneities present. Such microstructures play a prominent role in the dynamics of complex fluids, and in the case of hydrate slurries may lead to a large yield stress (τ_y), as the network of connected structures needs to be ruptured in order to make the material flowable. A significant yield stress can result

in formation of a hydrate plug, with associated blockage of a pipeline. The need for affordable, reliable and long-term methods for the prevention of hydrate plug formation and for prediction of start-up flow following pipeline flow shutdowns calls for a detailed understanding of the yielding behavior of water-in-oil emulsions under hydrate-forming conditions. In this work, we have measured the yield stress of cyclopentane hydrate slurries for varying water volume fractions.

For many hydrate systems, the solid hydrate formation takes place at temperatures below 4 °C at moderate to high pressure in the range of 1–10 MPa. However, high pressure is not necessary for all hydrate-forming systems. For example, cyclopentane (CP) and tetrahydrofuran (THF) form hydrates at atmospheric pressure [3]. As a model system, CP offers advantages over THF as it forms structure II hydrates which are commonly encountered in petroleum fields and it is immiscible with water as opposed to THF which is fully miscible with water. The immiscibility introduces the mass transfer limitations usually present in gas hydrate emulsion systems, making CP a suitable model material for study of properties of oil-field emulsions.

An alternative model system proposed to provide guidance in regard to oil-field emulsions is an ice slurry in an organic phase. Rensing et al. [5] studied the rheology of ice slurries formed from water-in-oil emulsions with average drop size of 1.5 μm for this purpose. Viscosity and yield stress of the ice slurries were measured at different volume fractions of fresh water and brine. Other

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studies have directly probed gas hydrate-forming emulsions, as in the work of Webb et al. [6] where a high-pressure rheometer with concentric cylinder geometries was used for rheological characterization of methane gas hydrates. This work used West African crude oil to make water-in-oil emulsions with mean drop size of 1.5 μm . Methane hydrate slurries were prepared from these emulsions at 0 °C and 10.4 MPa. Below 30% water volume fraction, there was no measurable τ_y . Between 30% and 50% water volume fractions, τ_y was less than 25 Pa and above 50%, τ_y was above the instrument limit of 3000 Pa.

There have also been a number of studies related to the rheology of hydrate slurries in general, but not specifically addressing the issue of yield stress. These studies provide context as they show rather strong dependence of rheological properties on the hydrate fraction, consistent with the behavior of the yield stress considered here. Camargo et al. [7] used a high-pressure cell for rheometric characterization of gas hydrate suspensions in asphaltic crude oils. The suspensions were formed from emulsions containing 15%, 30% and 50% (by weight) brine with typical drop diameter of 2.5 μm . A mixture of methane and ethane was used. The hydrate slurry obtained from 15% water fraction was found to be Newtonian, with neither shear thinning nor thixotropy, while hydrate slurries at 30% and 50% brine showed shear thinning and significant thixotropy. The non-Newtonian behavior was attributed to aggregation of hydrate crystals at lower shear rates and subsequent rupturing of these structures at higher shear rates. For the slurry with 50% initial brine, the system was reported to have significant bulk heterogeneity; this arose due to high solid fraction and growing particle diameter, which owing to density mismatch between the phases led to sedimentation of the solid particles. Such heterogeneity complicates the analysis of the material properties. There are a number of studies in which pipe flow is used to characterize the flow properties of hydrate slurries. Andersson and Gudmundsson [8] performed flow loop tests along with tube viscometry to characterize hydrate-in-water slurry. Flow rates and pressure drops were recorded for hydrate slurries flowing through straight pipe sections in laminar and turbulent conditions. The apparent viscosities of the slurries exhibited an expected increase at larger hydrate concentrations. Sinquin et al. [9] studied the flow behavior of hydrate slurries in laminar and turbulent flow conditions; at low Reynolds number, they reported a Newtonian behavior and relative viscosity was found to increase with increasing hydrate particle fraction. Sinquin et al. also mentioned a shear thinning behavior at high particle fraction and modeled it by incorporating an effective volume fraction. In the turbulent domain, the friction factor was reported to be an increasing function of the emulsion water volume fraction. Fidel-Dufour et al. [10] studied rheology of methane hydrate slurries obtained from water-in-dodecane emulsion in the presence of an anti-agglomerant additive in a flow loop reactor operating on a gas-lift principle. Experimental results were compared with a model which captures nucleation, growth and agglomeration steps of hydrate formation. The agglomeration of hydrate particles and water drops was assumed to be irreversible and was modeled using a population balance approach. The resulting hydrate aggregates were found to be porous with a reported fractal dimension of 1.8. A further flow loop study of note is that of Delahaye et al. [11], where the rheology of CO₂ hydrate slurry in a pressure- and temperature-controlled dynamic loop was considered for application in refrigeration. The concept of agglomeration-induced structures playing a prominent role in hydrate slurries noted above has received further attention. Colombel et al. [12] proposed a unified model for the agglomeration between hydrate particles in water-in-oil emulsion where they combined contact-induced agglomeration and shear-limited agglomeration to predict the evolution of viscosity of slurry during hydrate formation.

For the cyclopentane hydrate slurry, density matching (to eliminate segregation) and atmospheric pressure rheometry may be applied. Based on these advantages, Zyliftari et al. [4] studied the effect of salt loading in the brine component of a 40% (v/v) brine emulsion in which the organic phase contained cyclopentane. Using micro-differential scanning calorimetry to develop a hydrate-brine phase diagram, the thermodynamic conversion of water to hydrate particles was related to the measured rheological response. A crucial finding was that the maximum viscosity is obtained at 61–85% water to hydrate conversion while the maximum yield stress is obtained at 80% conversion – rather than at 100% conversion. This behavior suggests an influence of capillary bridges formed by unconverted water between hydrate particles.

In all of the hydrate flow studies mentioned above, the effects of wall slip have largely been overlooked. Wall slip effects are commonly observed directly or indirectly in flows of two-phase complex fluids, whether in pipes or in rheometers equipped with smooth geometries. Wall slip is a notable source of error in rheological measurements, as with wall slip the measured apparent shear rate is generally greater than the true shear rate [13–18]. Slip is typically due to a thin liquid-rich layer adjacent to the wall, which allows a large velocity gradient in this region, with a smaller value throughout the bulk of the flow. A commonly used method to eliminate wall slip effects is the use of a vane geometry, often in conjunction with a roughened cup [19,20].

From the foregoing, we see that properties of hydrate-forming emulsions have a strong dependence on the hydrate and residual water fractions, and there is a clear need for understanding of the stresses needed to maintain flow of these mixtures. To this end, we have examined the yield stress of CP based hydrate slurries formed from water-in-oil emulsions at varying water volume fractions. We studied the influence of wall slip by using a smooth cylindrical cup with a smooth bob and a roughened cylindrical cup with a vane rotor. The roughened cup with vane rotor, which is found to mitigate wall slip, is utilized to make a comparison of various yield stress measurement methods and develop a correlation of the data with the water volume fraction in the original emulsion. Decreasing shear stress ramp, oscillatory stress ramp, creep and nonlinear viscoelastic methods are used.

2. Materials and methods

2.1. Materials

The oil phase of emulsions in this study consists of 50% (v/v) cyclopentane and the remaining part is a mixture of two oils: light mineral oil (Fisher Chemicals) and Halocarbon 27. Halocarbon 27 is used to match the density of oil phase and aqueous phase in order to reduce the effects of sedimentation. The density and viscosity of Halocarbon 27 are 1.9 gm/cm³ and about 100 cP respectively, while the same for light mineral oil are 0.86 gm/cm³ and 46 cP respectively at 25 °C. A nonionic and oil soluble surfactant, sorbitan monooleate, commercially known as Span 80 (Sigma Aldrich) of density 986 kg/m³ is used. Deionized water is used as the internal phase and it is obtained from a Millipore QTM water purification system. All the materials were used as obtained without further purification. The temperature dependence of the viscosity of each liquid can be found in Peixinho et al. [3] and Zyliftari et al. [4]. The oil mixture with 0.1% by volume of Span 80 is prepared first. The emulsions of different compositions are prepared by a drop-wise addition of aqueous internal phase into the continuous organic phase, applying mechanical stirring using a homogenizer (IKA T25 digital Ultra-Turrax) operating at 7000 rpm for 5 min; a 30 ml emulsion sample is prepared in a standard 100 ml beaker. The samples were found to be stable against coalescence

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