SEMARAK ILMU
PUBLISHING
202103268166(003316878-P)

Journal of Advanced Research in Applied Sciences and Engineering Technology

Journal homepage:
https://semarakilmu.com.my/journals/index.php/applied_sciences_eng_tech/index
ISSN: 2462-1943

Optimization of Stable Water–Oil Emulsified Samples for Hydrate–Wax Interaction Studies

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ARTICLE INFO

Article history:
Received 1 January 2026
Received in revised form 20 January 2026
Accepted 25 January 2026
Available online 7 February 2026

Keywords:

Hydrate clathrate; wax precipitation; emulsion stability; bottle stability test

ABSTRACT

Hydrate and wax plugging pose major challenges in petroleum production, leading to flow disruption, blockages, and safety risks. In oil-dominated systems, emulsions are commonly formed, with hydrates developing at the interfaces of dispersed water droplets and wax precipitating concurrently within the continuous oil phase. These emulsions strongly influence hydrate–wax interactions, yet the role of emulsion characteristics remains underexplored. Achieving emulsion stability is important to ensure complete hydrate conversion and proper interaction with precipitated wax. However, optimum stability is difficult to evaluate, as multiple physical and chemical factors are interrelated. In this study, synthetic emulsions were prepared by dissolving octadecane (C_{18}) in heptane and emulsifying with water using Span 85 and Tween 85. The main objective was to generate stable emulsions that facilitated complete hydrate formation, while systematically evaluating the effects of surfactant concentration, surfactant type, wax ratio, and solvent type. Stability was evaluated using the bottle test, with viscosity and droplet size as supporting measures. Ten samples were prepared with varying formulations. Results showed wax content had the strongest impact: the 60:40 heptane:C_{18} sample maintained a stable emulsion for one hour, while the 80:20 ratio showed ~30% reduction. Higher wax content also increased viscosity (to 17.5 mPa·s), limiting droplet coalescence. Although interfacial tension suggested reduced stability, the findings confirmed that long-chain paraffinic components enhance stability even before wax precipitation. This study provides a basis for preparing stable emulsified oil–water systems, enabling more reliable hydrate–wax interaction research in flow assurance.

1. Introduction

Operating petroleum facilities is a challenging activity since it requires transporting fluid in long pipelines within extreme surrounding environment where the pipelines are positioned. In flow assurance studies, a critical concern is the deposition of solids originating from produced fluids, such as gas hydrates and waxes, which can accumulate on pipeline walls, joints, valves, and processing equipment.. Hydrate deposition is considered to be the primary challenge for deepwater tiebacks, as

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hydrates grow rapidly compared to other solid deposits [1]. Gas hydrates, or clathrate hydrates, are non-stoichiometric crystals formed when hydrate-forming components such as light hydrocarbon gases (i.e. methane, ethane or propane) and other non-hydrocarbon gases i.e. carbon dioxide (CO_2) or hydrogen sulfide (H_2S) are confined inside a cage-like structure of water molecules held together by hydrogen bonding [2]. The cage-like water structure that confines these gases forms thermodynamically under hydrate equilibrium conditions at high pressure and low temperature. For example, 1 m^3 of hydrate can liberate approximately 170 m^3 of gas [3] if the hydrate is thermodynamically destabilized, which can result in unintended movement of fluids or solids through the pipeline and may further enhance pipeline integrity concerns. However, there are a few cases where hydrate clathrate could form at atmospheric condition, for this instance, the usage of tetrahydrofurane and cyclopentane were used in generating hydrate, thus giving advantages in the study of adhesion force among hydrate clathrate [4-6].

Apart from the hydrate deposition, the presence of wax precipitation and deposition may also result in pipeline occlusion, compounding the challenge presented by hydrates. The formation of precipitated waxes is an example of a solid-liquid phase transitional phenomenon whereby long-chained paraffinic components, typically with carbon numbers between C_{20} and C_{80}, form precipitated solid wax at low temperature as a result of heat loss to the surrounding environment [7]. Paraffinic wax molecules can start precipitating below 90°C, where different paraffinic chains and types (straight, branched or ring structures) precipitate at variable temperatures [8,9]. As temperature reduces further below its cloud point, precipitated waxes start to nucleate, followed by clustering among wax particles that can deposit radially along the cold pipeline wall [8]. Continuous wax precipitation increases wax deposition on the wall; if it is left untreated, precipitation can increase the viscosity or decrease the cross-sectional area available for flow, thereby increasing the momentum requirement of fluid transport and associated risk of blockage [10-12].

Focusing specifically in oil-dominated systems, hydrate plugging has been established to follow four primary steps: (1) entrainment of water in the oil phase, forming an emulsion under the turbulent and high shearing flow rate; (2) nucleation of hydrate at the water-oil interface due to the high solubility of light hydrocarbon gases in the oil phase; (3) formation of a large hydrate particles, which begin to agglomerate due to strong cohesive forces between them; and (4) formation of a high viscosity slurry flow, eventually leading to hydrate deposition on the pipeline wall and plugging as depicted in Fig. 1.

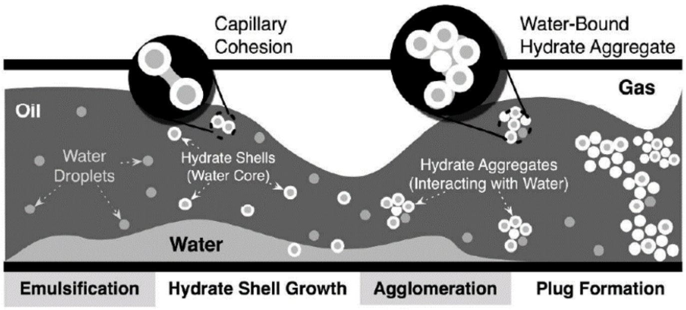

Fig. 1 Stages of hydrate plugging in an oil-dominated system [13]

The occurrence of hydrates in pipelines is often influenced by emulsions, which arise when water produced during oil extraction becomes dispersed as droplets in oil under turbulent flow conditions. The stability of these emulsions ultimately determines the rate of hydrate formation and dissociation. Concurrently, the presence of wax is also unavoidable as the results of heat loss to surrounding, forcing the fluid to operate below cloud point which indirectly leads to wax precipitation. In water-in-oil emulsions, differences in polarity and hydrocarbon–aqueous immiscibility drive the concurrent formation of hydrates and waxes in different phases. Hydrates generally emerge at droplet interfaces, while wax crystals precipitate in the bulk hydrocarbon phase, together creating compounded flow assurance risks [14].

Studies on hydrate–wax interactions remain limited, as most investigations have focused on either hydrates or waxes independently. The few available reports address potential synergistic effects and associated risks when both phases coexist [15]. Laboratory analysis conducted by de Oliveira, et al. [16] has examined the effect of wax properties on the possibility of hydrate plug formation. Results indicate that the severity of hydrate blockage increased because of oil gelation during pipeline start-up. In terms of thermodynamic modelling, Mahabadian, *et al.*, [17] reported an integrated thermodynamic model for predicting both hydrate and wax precipitation; the importance of cross-interaction between hydrate and wax becomes more substantial at deepwater operating conditions. This fundamental understanding is crucial to help in developing predictive models of the pipeline-plugging mechanism which is indirectly beneficial in optimizing pipeline operation and sizing.

Several studies have examined hydrate–wax interactions in relation to direct plugging consequences [16-18]. In addition, microscopic investigations have been conducted; for example, Zhou *et al.*, [19] quantified the cohesive forces between hydrate and wax particles using micromechanical force measurements, while another study demonstrated the influence of surfactants on hydrate growth at the water–oil interface. Among key findings from these reports is the different co-mingling interaction between hydrate and wax particles as a result of variation in wax concentration. For example, the adhesion forces between hydrate and wax particles was first decreased and increased when wax concentration was varied within 1-8 wt.% [18] and effectiveness of surfactant was found to be reduced with increasing critical wax content would directly reduce effectiveness of surfactant [19].

An in-depth investigation of hydrate-wax interactions presents a promising approach to addressing flow assurance issues. However, the effectiveness of such studies is highly contingent upon the stability of the emulsified system. This is contributed by a few factors which have direct or indirect interaction between each other, thus complicating the evaluation of this study. Therefore, this study aims to determine the highest emulsion stability of water-oil emulsified sample by considering multiple factors contributing to it. In this case, four different parameters are considered: surfactant concentration, type of surfactant used, the ratio between wax and solvent used and type of solvent used. These parameters were evaluated using three assessment approaches: bottle stability tests, viscosity measurements, and droplet size analysis via zeta measurement. To ensure effective comparison across samples, several conditions were held constant in accordance with standard analytical practices.

2. Methodology

In this proposed experimental procedure, an emulsified water-oil compound was prepared by combining both hydrate-based components alongside with wax compound. In this case, hydrate guest components of cyclopentane and heptane are used as hydrate guest components, alongside with water added into the emulsified sample. Unlike hydrate gas components such as light hydrocarbon gases (i.e., methane, ethane, propane etc.) which require high pressurized gas to form hydrate clathrate, cyclopentane has advantageous to form hydrate within atmospheric-based condition. On the other hand, the application of heptane acts as a based component that requires high-pressurized hydrate-based gases in assisting hydrate formation, which will be done in future experiment activities.

Concurrently, the presence of precipitated wax is introduced in hydrocarbon compound in the emulsified sample by dissolving solid pure paraffinic compound of C_{18} purposefully in the cyclopentane and heptane prepared earlier as the hydrate clathrate formation. The amount of C_{18} added into the dissolved is set at certain composition where the solid C_{18} must be dissolved completely in the solvent at room temperature. The usage of pure C_{18} is made to ease the evaluation of cloud point by pointing only one single peak for both WAT and WDT curves.

For emulsifying both the hydrocarbon compound and wax together, a synthetic surfactant of Span 85 and Tween 85 is added into the mixed compound before the mixture was homogenized evenly. Depending on the type of emulsion used, under induced cooling step, the hydrate will form at the water-oil interfacial phase, whereas precipitated wax form within hydrocarbon compound.

For the preparation of water-oil emulsified sample, a mixture of hydrocarbon mixture was homogenized with aqueous phase at ratio based on constant water cut (by volume). A hydrocarbon mixture consists of heptane (MW 100.20 g/mol, Sigma Aldrich) and solubilized high purity octadecane (C_{18}) (purity of 99%, Sigma Aldrich) where both liquid mixtures were prepared gravimatrically at molar ratio of 80:20 and 60:40, while an aqueous liquid mixture used in this experiment was a deionized water. The surfactants used in this experiment consisted of oil-soluble Span 85 (Sorbitane trioleate, Sigma-Aldrich, HLB ~1.8) and water-soluble Tween 85 (Polyoxyethylene sorbitan trioleate, Sigma Aldrich, HLB ~11), with their concentration adopted in this study ranges between 2% to 6% (v/v) relative to the total emulsion volume. All chemicals were used without any pretreatment procedures.

The emulsion was prepared by adding the desired volume of hydrocarbon mixture into 100 ml Schott bottle, with a ratio of 60:40 to deionized water maintained at constant volume. Due to solubility difference, Span 85 was added directly in the prepared hydrocarbon mixture, whereas Tween 85 was added into the aqueous liquid prior to the mixing process of both hydrocarbon and aqueous mixtures. Homogenization process was done using a homogenizer (Daihan HG-15 D) at the speed of 5000 rpm for ten minutes. The loaded hydrocarbon mixture was first set at homogenized condition before the deionized water was added gradually dropwise to guarantee uniform internal phase distribution. Upon the homogenization stage, the bottle was settled for one hour with images of the settling liquid were taken within 15-, 30-, 45- and 60-min intervals.

In a typical water-oil emulsified sample, the emulsion layer forms a middle layer that forms between the top layer of light density hydrocarbon compound and the bottom layer of aqueous phase. Physically, this emulsion sample forms top a thin, bubble layer which is sandwiched between a clear layer and the white bottom layer. Thus, it is difficult to clearly distinguish this layer from others. Therefore, for the convenience in obtaining quantitative measurement of the separated layer, the thickness of white layer was measured using Image-J software by dividing it with total layer of the whole homogenized sample.

Droplet size analysis of the emulsion system was conducted using the Zetasizer ZN3600, which can determine the size of particles and evaluate the stability of the given emulsion system. In this study, the emulsion layer that typically forms a middle layer of homogenized sample was extracted, and the extracted sample was placed in a quartz cuvette for about quarter of a full volume to ensure data precision. Subsequently, the cuvette was positioned in the instrument carefully to ensure proper alignment to the optics to avoid measurement errors. Before initiating the measurement, the sample parameters such as refractive index (RI) and viscosity, were input into the Zetasizer so that all conditions were pre-set. Each measurement comprises three repeated runs to facilitate average calculations and ensure accuracy. All final values were determined and documented. In general, smaller droplets are more stable due to a lower surface area to volume ratio where coalescence is slowed down by surfactants.

The viscosity of the emulsified water-oil systems was measured using a Vibro Viscometer (Model SV-10). This instrument operates on the principle of vibrating tuning forks, where changes in vibrational resistance correlate with the dynamic viscosity of the fluid. Viscosity plays a critical role in determining emulsion stability, as higher viscosity values are generally associated with reduced droplet mobility, minimized coalescence, and delayed phase separation.

Approximately 45 mL of the emulsion sample was transferred into a clean glass container. The container was gently elevated until the emulsion came into direct contact with the gold vibrating plates of the SV-10 viscometer. The viscometer was activated, and viscosity readings were continuously monitored until a stable value was obtained. The final viscosity value, expressed in millipascal-seconds (mPa·s), was recorded for each formulation and used for comparative analysis. The measurement of viscosity was done specifically for emulsion layer where the sensor was placed at the middle between the top and bottom layer of static sample.

Four different sets prepared for this experiment, covering set A for different concentration of surfactant (Span 85), set B for different type of surfactant used (Tween 85 and Span 85), set C for different wax ratio (for 100% heptane, wax to oil ratio at 20:80 and 40:60) and set D for different type of solvent used (heptane and cyclopentane), as shown in Table 1.

Table 1
Four different sets of samples, prepared based on different surfactant concentration (Set A), type of surfactant used (Set B), different wax ratio of heptane:C18 (Set C) and different solvent used in hydrocarbon mixture (Set D)

	Set A	Set B	Set C	Set D
	Different surfactant concentration	Type of surfactant	Different wax ratio	Different solvent used in hydrocarbon mixture
Concentration of surfactant used (wt%)	2 wt%, 4 wt%, 6 wt%	4 wt%		
Type of surfactant used	Span 85	a) Span 85 b) Tween 85	Span 85	Span 85
Different wax ratio in hydrocarbon mixture	Heptane: C_{18} at 80:20 by mol	Heptane: C18 at 80:20 by mol	a) Heptane: C_{18} at 80:20 by mol b) Heptane: C18 at 60:40 by mol c) Pure heptane	Heptane: C_{18} at 80:20 by mol
Type of solvent used	Heptane	Heptane	Heptane	a) Heptane: C_{18} at 80:20 by mol b) Cyclopentane: C_{18} at 80:20 by mol
Water cut ratio (vol%)	40% v/v			

As the basis of the sample preparation, all ten different samples of homogenized sample were set at consistent water cut of 40%. Although there are many other possible factors that could affect emulsion stability, only four different factors were selected with consideration that these factors have significant role in affecting emulsion stability. However, note that the sample total volume among all ten different sample was slightly varied with maximum volume was set at 100 ml, considering that all the measurements were independent to the sample volume.

The intended sample should produce a water-in-oil emulsion sample, where the usage of Span85 is expected to produce W/O emulsion due to its high HLB. However, for the sake of full overview, Tween 85 was used in this experiment. As for the sample Set A, the concentration used is common range of concentration used in this field of study, but for simplicity, the effect of critical micelle concentration (CMC) was omitted.

3. Results and Discussion

Based on Fig. 2, the highest emulsion stability was achieved by sample Set C (wax ratio of 60:40) with the thickness of bottom layer remained unchanged within one hour (almost 100%), whereas the lowest emulsion stability was recorded by sample Set A for the concentration of Span 85 at 2 wt.% with the lowest thickness of bottom layer was recorded at 57% at 60 min. The highest emulsion destabilization was observed for sample Set C (wax ratio of 80:20) with reduction of almost 27% with the period of an hour. Fig. 2 also shows that majority of emulsion destabilization centered within the thickness of bottom layer to be at 70%-60% by the end of 60 min. The slope of a line indicates the rapid change of emulsion stability, in the case of Set A (different Span 85 concentration), improvement of emulsion stability was expected with slight improvement in the case of surfactant at 2 wt.% (57%), 4 wt.% (61%) and 6 wt.% (64%). As for the observation of Set C, improvement of emulsion stability was recorded by the increase of C_{18} ratio, whereby changing from 20 mol% to 40 mol%, the sample drastically improved its stability from 75% to almost 100%. Drastic improvement of emulsion stability was shown by data at Set B, where the sample containing Tween 85 recorded the second highest stability at 91% whereas a sample containing Span 85 at identical concentration generated stability for only 61%.

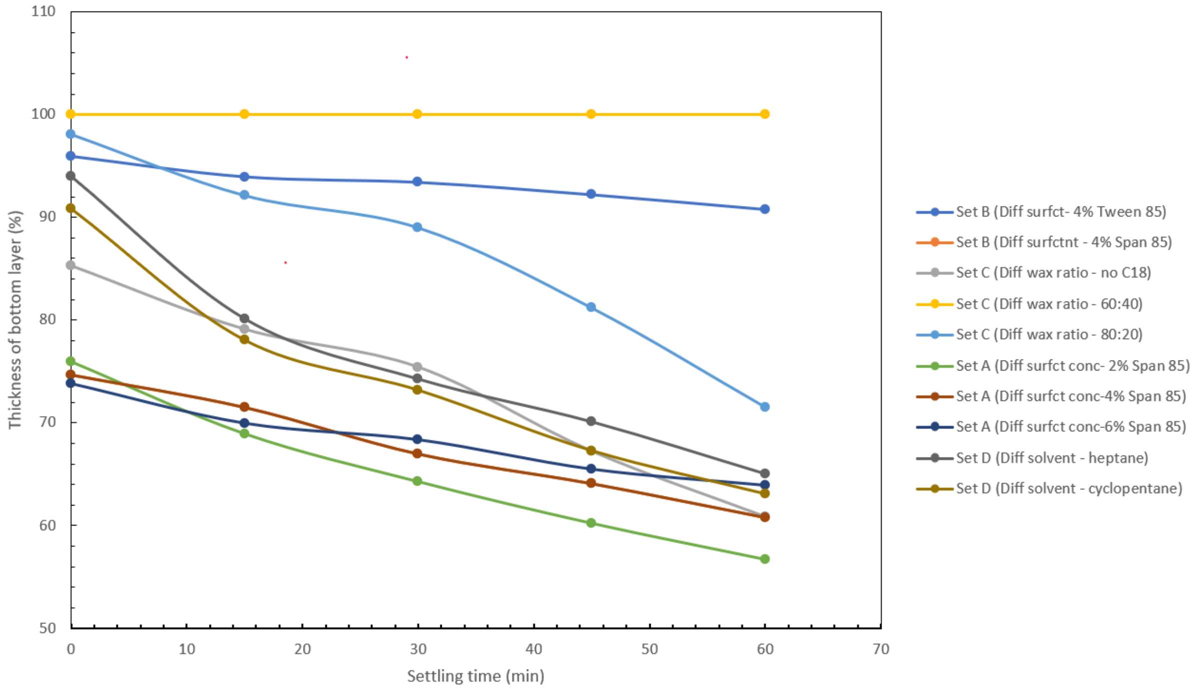

Fig. 2 Thickness of bottom layer of emulsified sample of four different set of samples. The connecting line acts as a guidance only. Note that the data of Set B (4% Span 85) and Set A (4% Span 85) are identical with both data overlap

Fig. 3 shows various droplet size measurements obtained using Zeta sizer, where measurement was done at the final period of emulsion stability at 60 min. The largest diameter of droplet was recorded for Set A at Span 85 concentration of 4 wt.% at about 1400 nm, while the lowest droplet was observed at Set B for Tween 85 at 4 wt.% (600 nm). Uneven trend was recorded for Set A where slight increase of droplet diameter was observed at Span 85 4 wt.%. Likewise, inconsistent trend of data was recorded for Set C where among three different samples used, the sample of 80:20 wax ratio showed decreasing trend before the size increases back at 60:40 wax ratio.

Relative to the emulsion stability, large diameter of droplet is associated with high destabilization since large droplets tend to coalesce and form separate layers with respect to its density. Here, the increment of surfactant concentration (Set A) produced relatively small variation of its droplet size within 1400-1000 nm, even with an odd increment of droplet size at 4% surfactant concentration, contrary to the expected results if higher concentration of surfactant was used.

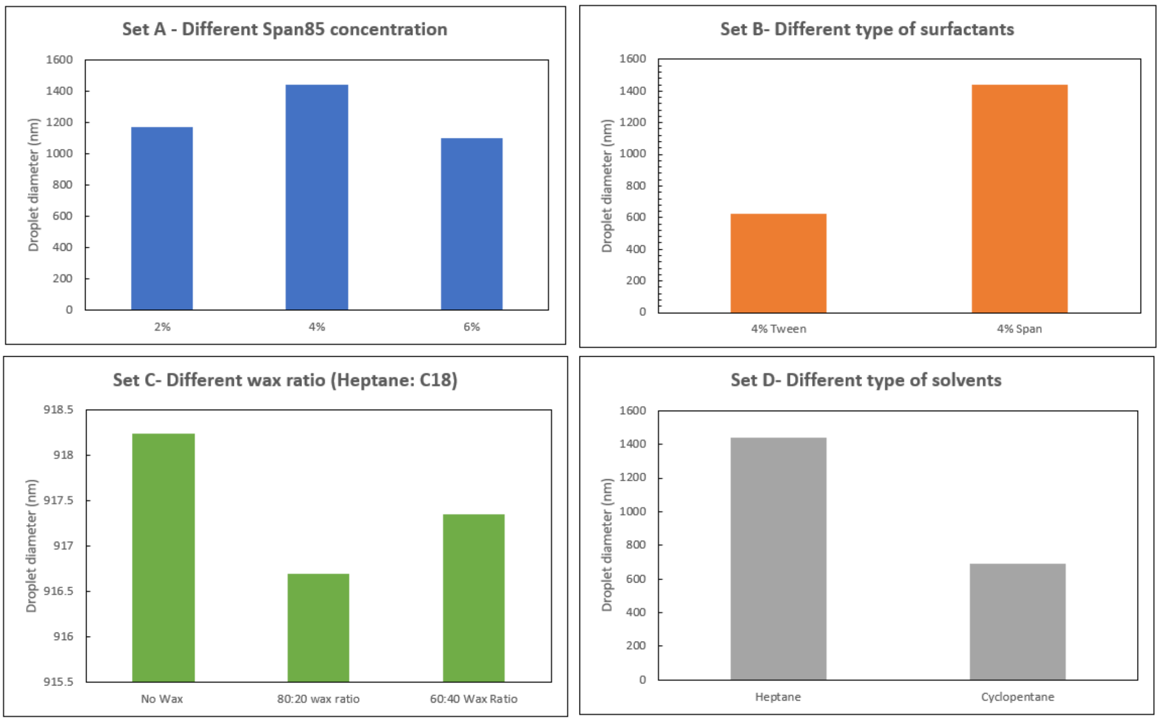

Fig. 3. Diameter of droplet measured using Zeta sizer of four different set of samples

This may indicate that the concentration may reach critical micelle concentration (CMC), which contributes to relatively unchanged trend of droplet. In parallel assessment, the small droplet indicated by Set B (Tween 85 4%) is in line with high emulsion stability, as presented in Fig. 3. As expected, the emulsion produced from the sample is made by oil-in-water (O/W) emulsion in which the dispersed droplets are made from oil within continuous phase of water. The assumption is based on HLB value of Tween 85 which is relatively favored to form oil-like surfactant, where, unlike Span 85 commonly used in this study, favors to form water-like droplets [20].

Fig. 4 shows viscosity profile of emulsion layer measured using viscometer for four different sets of samples. The highest viscosity was recorded by set C (for wax ratio heptane: C_{18} at 60:40) at 17 mPa.s, whereas the lowest viscosity was obtained for sample set B (using Span 85) at roughly below 6 mPa.s. Gradual increment of viscosity could be observed for all samples at Set A, where the lowest Span 85 concentration (2 wt.%) measured to be 7 mPa.s and gradually increased to about 14 mPa.s at Span 85 6 wt.%. Likewise, gradual increment could be observed at all three sample of set C, ranging between 16 mPa.s to 17.5 mPa.s. However, no significant difference was observed for sample of different surfactants (Span 85 and Tween 85), where the variation was recorded at merely 6 mPa.s and 7 mPa.s. Similarly, no significant change could be observed for set D when there is variation in solvent of cyclopentane and heptane was used.

The presence of high viscosity particularly for high surfactant concentration is expected as the presence of smaller water droplet generated more resistance for fluid flowability [20], where it is shown by results of set A. However, at the same amount of surfactant used at 4 wt.% (at 10 mPa.s), higher viscosity could be achieved almost doubled at set C for higher amount of C_{18} in wax ratio (60:40 mol%) at 17 mPa.s. Higher viscosity is commonly associated with the presence of long-chain paraffinic components, where its existence within continuous phase reduced flowability of sample that indicate from yield strength measurement.

Higher viscosity values, particularly in emulsions stabilized with Tween 85, indicate greater structural resistance to gravitational separation and droplet coalescence [21].

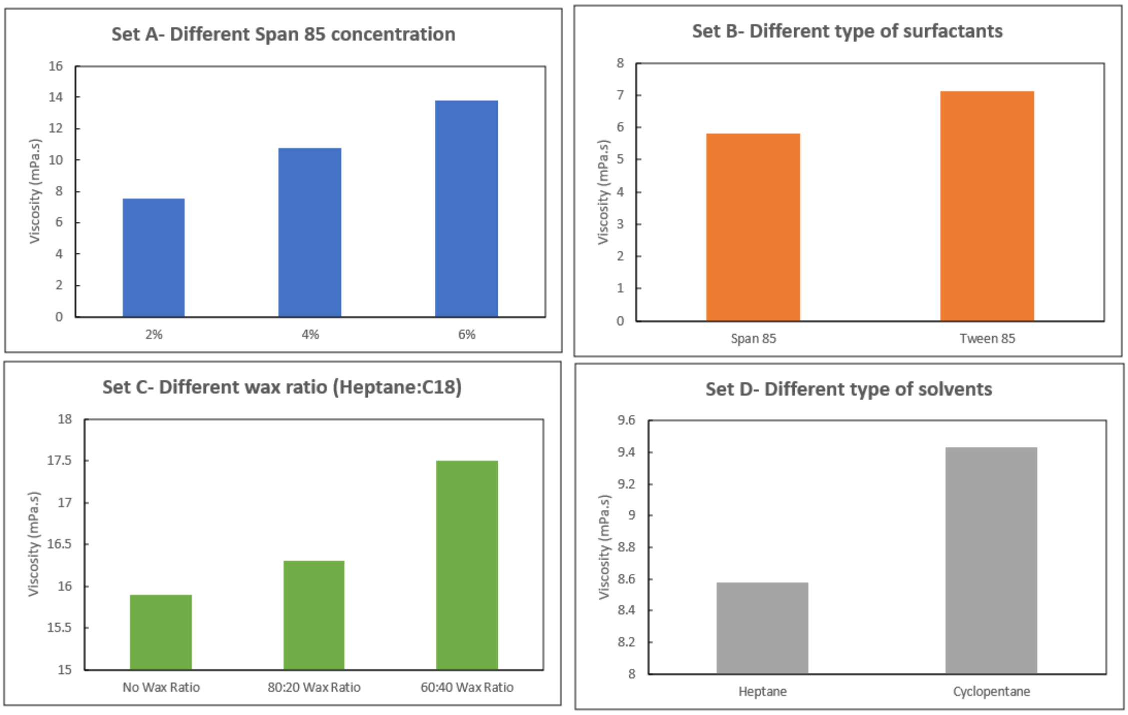

Fig. 4 Viscosity measurement of emulsion layer of four different set of samples

This is consistence with the tendency of Tween 85 to produce O/W emulsion which generally exhibit higher viscosities compared with the W/O emulsions formed by using Span 85 [22,23]. High viscosity does not always mean a more desirable stability. It can either stabilize the emulsion against separation or, if excessive, can create plugging risks by turning the system into a rigid gel.

3.1 Stability, Droplet Size and Viscosity

Observing three different set of results presented earlier, the emulsion stability reflects the contribution of both the droplet size measurement, as well as the viscosity measurement. Upon completion of homogenization stage, the sample was treated as a static emulsified sample where both immiscible fluids of hydrocarbon compound and aqueous phase would tend to separate by coalescing among their respective components, thus forming different layers before the sample reaches equilibrium. However, in the presence of surfactants, the amphiphilic molecules of surfactants reduce interfacial tension, thus forming barrier for both immiscible aqueous and hydrocarbon liquids to coalesce. In the case of water-in-oil (W/O) emulsion, the hydrophilic head (water loving head) will orient into water droplet, and the hydrophobic tail will be facing outward into the oil. Conversely, the orientation is reversed for the case of (O/W) emulsion, depending on the difference in hydrophilic lipophilic balance (HLB). Besides difference in HLB, the emulsion stability of an emulsified sample depends on both physical and chemical properties of continuous-dispersed phase.

In the above case, the presence of a long-chain paraffinic component of C_{18} was observed to be the primary cause of improvement in emulsion stability, which is in agreement to the results of the bottle stability test and viscosity. The results of the bottle stability test (Fig. 3) indicates that additional amount of surfactant from 2 to 6 wt.% tested at the same wax ratio of 60:40 has effect less that then the case with higher amount of wax at 60:40. It shows that, the presence of higher amount of paraffinic component of C_{18} along with the surfactant suppresses dispersed droplets (in the case of Span 85 is water droplets) from coalesce and separate. Additionally, the viscosity results presented in Fig. 4 showed that higher viscosity of Set C particularly for sample at 60:40 wax ratio was recorded (17.5 mPa.s), contrary to the rest of other sets tested. As for the observation of droplet diameter, Set C was observed to be in intermediate size compared to other sets, with droplet size ranging between 915-920 nm regardless of different wax ratio.

Unlike other cases which reported the presence of crystallized wax that helps retaining the emulsion stability [24,25], this current work was done above the expected cloud point, where no crystallized wax could exist as continuous phase of emulsified sample as the experiment was conducted at temperature above cloud point of the hydrocarbon compounds. The obtained results might be contributed by higher viscosity in continuous phase that minimizes coalesce among water droplets [26,27] where a high viscous fluid acts as a resistance for the movement of dispersed droplets. However, the high viscosity may not significantly contribute to the smaller diameter of droplet, since a smaller droplet size may give the opposite in emulsion stability [28], which consequently does not give complete picture of total emulsion stability.

Within these ten different water-oil emulsified samples, a sample that uses 4 wt.% Span 85, wax ratio at 80:20 and heptane is classified as the base case since the sample exists in all four different cases due to its similarity. Despite this setup, inconsistent results were expected as the samples were prepared by different individuals with slight variation in their apparatus. For example, in the case of Set C, the based case sample generated discrepancy on both droplet diameter measurements (916.5 nm compared to the actual to be 1400 nm). In contrast, the bottle stability test and the viscosity measurement are both subjected to discrepancy due to the variation in visual assessment and the position for measuring exactly the emulsion layer. Acknowledging this setback, such variation is mostly anticipated due to the dynamic and continuous separation that takes place upon homogenization stage. Nonetheless, focusing on the sample at Set C, additional amount of paraffinic component generated significant reduction of droplet diameter and increase in viscosity value where these outcomes are in-line with the hypothesis.

4. Conclusions

Based on the results presented earlier, the results confirm that higher paraffinic wax content enhances emulsion stability, as demonstrated by sample of Set C which maintained approximately 90% stability during the bottle stability test. This result correlated with increased viscosity at 17 mPa.s. at 60:40 heptane: C18 ratio which restricted droplet coalescence. Although Set C showed an intermediate droplet size in about 900 nm, the stability did not directly correlate with size alone. This indicates that droplet size is insufficient predictor of emulsion stability, and the viscosity of the continuous paraffinic phase plays a decisive role. In addition, these findings suggest that multiple interrelated physical factors must be considered when assessing emulsion stability and providing a more reliable structure for studying hydrate-wax interactions in flow assurance.

Acknowledgement

The authors wish to express their sincere appreciation to the UiTM Research Management Centre (RMC) for the support provided under the Fundamental Research Grant Scheme – Early Career (FRGS-EC) (FRGS-EC/1/2024/TK05/UITM/02/24). Heartfelt thanks are also extended to the laboratory support staff, Madam Azizan Din and Madam Meliza, from the Faculty of Chemical Engineering, UiTM Shah Alam, and the Faculty of Pharmacy, UiTM Puncak Alam, for their dedicated assistance and continuous guidance to the Final Year Project (FYP) students throughout the laboratory research activities.

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