Effect of Crystal Modifiers and Dispersants on Paraffin-Wax Particles in Petroleum Fluids

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Summary

Petroleum fluids from shale light-oil and gas/condensate reservoirs generally have a high content of normal paraffins. Paraffin-wax deposition is among the challenges in shale gas and oil production and in offshore flow assurance. Low-dosage chemical additives can be effective in paraffin-wax mitigation because of their high efficiency and economics. These additives are divided into broad categories of crystal modifiers and dispersants with vastly different molecular structures and mechanisms in wax-crystal-particle stabilization and wetting. This investigation focuses on the understanding of the differences in the aggregate size and morphology of chemical additives, and it centers on (1) wax-particle sedimentation from diluted petroleum fluids in vial tests, (2) wax-crystal-particle-size distributions and morphology by dynamic light scattering (DLS) and polarized-light microscopy, and (3) the wetting state from the effect of water. In two of the three petroleum-fluid samples used in this work, there is no visible precipitation at the bottom of the vials at temperatures below the wax-appearance temperature (WAT). The microscopic image of fluids along the length of the tube shows that the waxparticle size and intensity increase from top to bottom. To observe precipitation, we dilute the crude with a hydrocarbon such as *n*-heptane. The sedimentation of wax is then observed. The petroleum fluids used in this work have very low asphaltene content, and there is no complication from asphaltene precipitation. Our study shows that a small amount of crystal modifier and dispersant can reduce crystal-particle size to the submicron scale, and change the crystal morphology. We investigate the differences in the mechanisms of dispersants and crystal modifiers in bulk. Water, which is often coproduced with petroleum fluids, can increase the effectiveness of dispersants significantly by altering the wetting state of the wax-particle surface. Such enhancement is not found in crystal modifiers. Both additives affect the rheology of petroleum fluids.

Introduction

Petroleum-fluid production from shale reservoirs, as well as in deep water, often encounters challenges from paraffin-wax deposition (Becker 2000; Radulescu et al. 2008; Aiyejina et al. 2011; Sarica and Panacharoensawad 2012; Huang et al. 2015). Paraffin wax is a major component in some petroleum fluids and refined middle-distillate products (e.g., diesel, kerosene, and heating oil). Wax consists of linear (*n*-paraffin) and branched hydrocarbon molecules with more than 16 carbons (Abdallah and Weiss 2000; Aiyejina et al. 2011; Huang et al. 2015). Wax deposition commonly occurs along the pipe walls when the temperature drops below the WAT or cloud point (Aiyejina et al. 2011; Sarica and Panacharoensawad 2012; Huang et al. 2015). The formation of crystalline depositions is primarily dependent on *n*-alkane sizes (Baltzer Hansen et al. 1991; Singh et al. 1999; Sarica and Panacharoensawad 2012). The waxes are stacked platelet crystals with sizes of hundreds of micrometers that deposit on the pipe walls if no inhibitor is applied (Abdallah and Weiss 2000; Aiyejina et al. 2011; Radulescu et al. 2012; Sarica and Panacharoensawad 2012; Huang et al. 2015). Wax deposition lowers the production rate, requires frequent pigging, and increases costs and risks.

The traditional methods to remove paraffin-wax depositions include hot oiling and hot watering in land operations; pigging for flowlines and dry-tree wireline access which allows the removal of soft waxes in offshore operations (Mansure and Barker 1992; Becker 2000; Aiyejina et al. 2011; Al-Yaari 2011). Use of chemical additives may improve treatment efficiency. There are two types of chemical additives in wax mitigation: crystal modifiers (also called wax inhibitors) and wax dispersants (Petinelli 1979; Richter et al. 1997; García 2000; Leube et al. 2000; Monkenbusch et al. 2000; Machado et al. 2001; Machado and Lucas 2002; Ashbaugh et al. 2002, 2005; Schwahn et al. 2002; Radulescu et al. 2003, 2004, 2006, 2012; Guo et al. 2004a, b, c, 2006; Marie et al. 2005; Tinsley et al. 2007; Jafari Behbahani et al. 2008; Xu et al. 2009, 2013; Li et al. 2010, 2012; Yi and Zhang 2011). We will briefly discuss the chemistries of the two chemical additive types, and state the way they work and specify the difference.

Crystal modifiers are mostly specialty synthesized copolymers, either block copolymers or random copolymers, which interact with wax crystallization to reduce the wax deposition (Radulescu et al. 2012). A recent review (Wei 2015) with a focus on crystal modifiers discusses the type of polymeric compounds used in wax mitigation. The review states that the size of wax crystals reduces significantly from the application of polyaminoamide material, but the size reduction is not quantified. Later, we will discuss the class of polymers that has been used. Wax-like segments in crystal-modifier molecules cocrystallize with the native paraffin waxes in the petroleum fluid to reduce crystal size and to modify the morphology (Ashbaugh et al. 2002; Radulescu et al. 2003, 2012). Other segments, such as the branched alkane chains or hydrophobic groups, do not crystallize in the petroleum fluid. They provide steric hindrance on the crystal surface that can prevent crystal growth and aggregation. From these effects, paraffin-wax crystals have a lower tendency to aggregate.

Wax dispersants are usually surfactants, which can adsorb onto wax-crystal and pipe surfaces to alter wettability to more-waterwetting and to lower wax adhesion to the surface (Dobbs 1999). Reports on wettability measurements are limited.

Crystal modifiers include ethylene-vinyl acetate copolymers (EVA), polyethylene-poly(ethylene-propylene) diblock copolymers (PE-PEP), poly(ethylene-butene) copolymers (PEB), poly(maleic anhydride amide co- α -olefin) (MAC), and their derivatives. The effectiveness of these additives is a function of vinyl acetate (VA) content, molecular weight and polydispersity, and petroleum-fluid compositions (Petinelli 1979; Machado et al. 2001; Machado and Lucas 2002; Ashbaugh et al. 2005; Marie et al. 2005; Jafarnia Behbahani et al. 2008; Jafari Ansaroudi et al. 2013). The optimal VA content is approximately 30 wt% (Machado et al. 2001; Machado and Lucas 2002), which exhibits higher effectiveness with longer paraffins (Machado and Lucas 2002; Ashbaugh et al. 2005). Scanning-electron-

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microscope (SEM) images show that EVA changes wax particles from plate-like to more-compact spherical morphology (Ashbaugh et al. 2005; Jafari Ansaroudi et al. 2013). However, the efficiency is reduced by asphaltenes (Machado and Lucas 2002; Jafarnia Behbahani et al. 2008). PE-PEP can self-assemble to promote nucleation of long-chain paraffins covered by amorphous PEP brushes (Leube et al. 2000; Monkenbusch et al. 2000). Inspired by PE-PEP, some authors have used a more effective PEB (Schwahn et al. 2002) to change crystals from plate-like to rod-like or shuttle-like structures (Guo et al. 2004a, c, 2006; Tinsley et al. 2007). It is also reported that hydroxyl-grafted PEB (PEB-OH) is more effective in asphaltene-contained petroleum fluids than PEB (Guo et al. 2004a). MAC polymers have been used to mitigate wax deposition (Son et al. 1993; García 2000). These polymers can either self-assemble to nucleate the paraffin crystallization or cocrystallize with paraffins to reduce crystal growth (Xu et al. 2009; Li et al. 2010). For waxy crudes containing asphaltenes, MAC is reported to be more effective than PEB in improving the flowability (Li et al. 2012). Singhal et al. (1991) note two empirical rules for choosing crystal modifiers: The side-chain length of the alkyl ester should have carbon numbers comparable to those of paraffin components, and the melting point should match that of the wax to limit the growth of the crystals. Crystal modifiers have been successfully used in many applications worldwide. Woo et al. (1984) report the success of a blend of crystal modifiers in a controlled-release matrix form in long-term paraffin-deposition control. A squeeze technique was developed to inject crystal modifiers for field applications (Dobbs 1999; Halim et al. 2011). Swanson et al. (2005) report the successful use of the combined hydrate kinetic and paraffin inhibitors in a deepwater pipeline with a high water cut in the Gulf of Mexico.

Dispersants are commonly formulated from chemicals such as alkyl sulfonates, alkyl aryl sulfonates, alkyl phenol derivatives, fatty amine ethoxylates, ketones, terpenes, polyamides, and naphthalene (Dobbs 1999). Wax dispersants have been in use for decades, but published literature on these chemicals is limited. No systematic investigation has been made on the effect of the dispersants and crystal modifiers on crystal size, with or without water.

There are differences between crystal modifiers and dispersants. One key difference between crystal modifiers and wax dispersants relates to the functional groups such as phenol derivatives in dispersants where water may have a major effect. In this work, we will show the effect of water on both crystal size in the bulk and in adsorption on metal surfaces. Other differences will be discussed in the Results section.

Dispersants and crystal modifiers have attracted much interest in the past few decades, but the mechanisms are not yet fully understood. The main objective of our work is a systematic investigation on crystal size and wetting-state alternation by wax dispersants and crystal modifiers in waxy petroleum fluids. Our investigation also includes fluid rheology. Fluid rheology has been extensively studied in the past (Pedersen and Rønningsen 2003). In this work, we propose a simple sketch to show the mechanism of action by crystal modifiers and dispersants.

Experimental

Materials. In this work, three petroleum fluids (AG-1, -2, -3) from shale formations in Argentina were investigated. The samples have paraffin content of 7.6, 6.7, and 4.5 wt%, respectively, measured by the UOP-46 method. Saturate content is as high as 90 wt%. The approximate WAT of these petroleum-fluid samples is between 36 and 45° C, measured by a rheometer at a 0.5°C/min cooling rate. The fluid samples were kept above 50°C before the tests. The relevant properties of the petroleum fluids are presented in **Table 1**. The asphaltene content of fluid AG-1 is lower than that of the AG-2 and AG-3 samples. The latter are somewhat darker than AG-1. We investigated nine chemical additives (dispersants A04 through A06 and crystal modifiers B01 through B06) in this work. The dispersants (A04 through A06) are polyalkylated phenols with 50-wt% active components in aromatic solvents. The crystal modifiers B01 through B06 are copolymer esters with 37-wt% active components in aromatic solvents. The additives are oil-soluble/dispersible, and are composed of carbon, hydrogen, and oxygen only. They are harmless to oil-refinery operations. *n*-Heptane is 99% pure.

Crude	Density (g/cm ³) at 20°C	Viscosity (cp) at 50°C	Viscosity (cp) at 15°C	Wax (wt%)	Asphaltene (wt%)	WAT (°C)
AG–1	0.82	2.97	12.2	7.6	<0.1	44.5
AG–2	0.83	3.18	19.9	6.7	0.22	40.5
AG–3	0.83	3.14	12.4	3.5	0.15	36.0

Table 1-Relevant properties of three petroleum-fluid samples.

Apparatus. The wax-particle-size distributions were measured by DLS at 20° C. The wax images were taken using a microscope camera system with polarized light. The rheological properties were characterized in the temperature range of 5 to 50° C by a modular compact rheometer using the plate/plate method.

Procedure. *Wax Sedimentation in Vials.* Two of the petroleum fluids used in this work are unusual with respect to wax precipitation. In samples AG-1 and AG-2, we did not observe wax precipitation in the vials even after 1 week when the temperature was some 15° C below the WAT. We then mixed the petroleum fluids with *n*-heptane and observed wax precipitation in a short time. In Appendix A, we present microscopic images of different samples along the vials to show that, indeed, wax particles are there but do not sediment. However, in flow testing the same crudes that do not show precipitation in vials, we do observe wax deposition. The work on flow and deposition will be submitted for publication soon. In the vial experiments with *n*-heptane, a homogeneous warm crude sample AG-1 (>50°C) was mixed with *n*-heptane in a 15-cm³ centrifuge tube at 15° C. The mixing ratio was $0.5 \text{ g}:10 \text{ cm}^3$ or $1 \text{ g}:10 \text{ cm}^3$ except for those samples described in Appendix A. The tubes were put on a rack after thorough mixing.

In this work, we used nine additives for wax-sedimentation investigation, A04 through A06 and B01 through B06. as stated previously. The dosages refer to their concentration in *n*-heptane, in the range of 50 to 2,000 ppm (ppm is in weight basis throughout this paper). All the vial tests were repeated, and similar observations were made. In Appendix A, repeated results are presented that should be considered as qualitative.

Wax-Crystal-Particle Sizing. Homogeneous warm petroleum-fluid sample AG-1 (>50°C) was mixed with *n*-heptane in a 7-cm³ glass vial. The mixing ratio was 0.5 g:5 cm^3 . Sizing measurements were conducted at 20°C. Before size measurements, the vials were kept above 50°C. Timing started after the vial was placed in the measuring chamber. The temperature reached 20°C in less than 1 minute. The measurements were taken at different time points without disturbing the vial.

Microscope Imaging. Wax crystals from different mixtures were observed and imaged under a materials microscope at room temperature using polarized light. The sample was prepared by placing one drop of the crude/n-heptane mixture from vial tests on a glass slide. The petroleum fluid at 50°C was mixed with n-heptane at room temperature, and after 60 minutes, the vial was shaken before sampling, and the droplet was taken from the middle section.

Viscosity Measurement. In this work, we used a rheometer to study the temperature dependency of the viscosity of the mixture of the crudes and additives, and to obtain WAT. We did not add *n*-heptane to the crudes in viscosity measurements. Kok et al. (1996) have reported agreement among three WAT-measurement techniques: differential scanning calorimetry, thermomicroscopy, and viscometry. WAT depression has been reported by various wax additives in a viscometer (Pedersen and Rønningsen 2003).

A homogeneous warm crude sample (>50°C) was loaded after the rheometer compartment was preheated to 50°C. A plate/plate method (top plate CP 50-2, diameter 50 mm) was used at a fixed rotating speed of 100 rev/min. The temperature then dropped to 5°C at a rate of 0.5° C/min, and the viscosity was recorded. The change of viscosity slope with temperature provides WAT. The WAT and viscosity temperature dependency were investigated as functions of chemical additives. The use of viscosity data may not be an accurate method for estimating WAT, but our results provide an adequate approximation.

Contact Angle and Effect of Aqueous Phase on Crystal Size. We first present contact-angle data and then the effect of aqueous phase on crystal size. Three substrates were used for contact-angle measurement: stainless steel, stainless steel coated with A04, and stainless steel coated with B04. The coating process was as follows. A small piece of steel was dipped into the 500-ppm A04 (or B04) and toluene solution. After 30 minutes, it was pulled out and fully air dried. Droplets of 5-wt% NaCl brine were then placed on the substrates for contact-angle measurement. The contact angle is reported on the basis of six measurements.

Resembling vial tests, AG-1 (with or without additives) was mixed with *n*-heptane. The ratio of AG-1 to *n*-heptane was $0.5 \text{ g:}5 \text{ cm}^3$. Then 0.1 cm^3 of 5-wt% NaCl brine was added. The vials were shaken for 2 minutes and left still. The aqueous phase separated from the oil phase completely after 5 minutes. The oil phase was then characterized by DLS for particle-size-distribution measurements. Microscope imaging was also performed on the oil phase.

Results and Discussion

The three major challenges in flow assurance include paraffin waxes, asphaltenes, and gas hydrates. Paraffin molecules might form small crystals in a petroleum fluid when the temperature is below the WAT. Individual crystals might aggregate and grow into larger particles, which might suspend in the fluid or might form a separate liquid phase containing wax particles. Asphaltenes might also precipitate from a petroleum fluid, aggregate, and precipitate. Therefore, there is a certain similarity between paraffin waxes and asphaltenes. Hashmi et al. (2010) studied the sedimentation behavior of asphaltene suspensions in n-heptane with addition of various dispersants. They found that effective dispersants reduce asphaltene-particle size, and greatly reduce the sedimentation. In this work, we use the same idea to study the wax sedimentation in vials for the screening of chemicals because wax deposition is also the formation of wax crystals and adsorption onto the surface. The paraffin-wax sedimentation in petroleum fluids can be very slow because of relatively high fluid viscosity (compared with *n*-heptane) and because the densities of wax and the petroleum fluid are close. As stated previously, to observe the sedimentation of the wax crystals, we mix AG-1 and n-heptane with the ratio of 1 g:20 cm³, which decreases the fluid-phase viscosity and density. Because the crude has very low asphaltenes and solubility of waxes is low in *n*-heptane at low temperature, there is no complexity from the introduction of *n*-heptane. As shown in Fig. 1a, a significant amount of wax is observed at the bottom of the tube after 20 minutes at 15°C. The amount of sediment increases over time. The sedimentation tests are also performed with crystal modifiers B01 through B06, among which B04 is the only effective additive, as illustrated in Fig. 1b. Adding a small amount of B04 (as little as 25 ppm) can reduce paraffin-wax sedimentation significantly. Wax sedimentation is observed on the cone sidewall at 25-ppm B04, which may be an indication of smaller particle sizes compared with the reference fluid with no additive. Fig. 1c presents the results by adding dispersants A04, A05, and A06 at a dosage of 1,000 ppm. Similarly, noticeable wax sediments are observed in all three tubes after 60 minutes. However, the amount of sediments is less at 1,000 ppm of A04 and A05, unlike A06. These observations suggest that A04 and A05 reduce sedimentation in the same period of time significantly; A06 is not effective. On the basis of the results from vial testing, wax dispersant A04 and crystal modifier B04 show effectiveness in reducing wax-crystal sedimentation. These two additives were investigated further by other measurements. We would like to mention that, in addition to particle-size reduction, the tendency of crystals to adhere to the surfaces would affect the effectiveness of additives.

Because of the low dosage of additives used, their effect on phase equilibrium is negligible. However, it was observed that the sedimentation in the same period of time differs dramatically. Such an effect of additives can be explained only by small wax-particle sizes. The sedimentation velocity (v_S) is governed by the particle shape and size (radius *a*), the fluid viscosity (μ), and the density differences between the particles and the fluid ($\Delta \rho$). For a single sphere, the velocity is described by Stokes' law,

$$v_S = \frac{2}{9} \frac{\Delta \rho g a^2}{\mu}$$

This formula shows the pronounced effect of particle size on sedimentation velocity. It also shows the effect of viscosity and the density difference on velocity. In diluted n-heptane, the viscosity reduction is from 12 cp to approximately 0.4 cp at room temperature. The density difference between the wax particles and crude and between the wax particles and n-heptane is also significant. As a result, there may be a velocity increase of two orders of magnitude in dilution with n-heptane.

Next, we use DLS to measure particle size in mixtures with A04 dosage from 0 to 2,000 ppm. The size distributions at 10 and 60 minutes are presented in **Fig. 2.** For the reference test (AG-1), the wax particles grow to $1.35 \,\mu\text{m}$ in 10 minutes, and $1.6 \,\mu\text{m}$ in 60 minutes. In comparison, it is found that the particle size decreases significantly by adding A04. At 10 minutes, the wax particles have smaller mean size and narrower distribution as the A04 concentration increases. For instance, at 2,000-ppm A04, the mean size is only 72 nm at 10 minutes, as shown in Fig. 2a. The dependence of mean size on A04 concentration changes at 60 minutes, as shown in Fig. 2b. The mean size is 544 nm at 500 ppm. At 1,000 and 2,000 ppm, the mean sizes are 630 and 639 nm, respectively. The size distribution becomes broader at a longer time. The same trend is also observed for B04, as presented in **Fig. 3**. At 10 minutes, the mean size is only 57 nm at 500 ppm of B04. However, the mean size becomes 613 nm at 200 ppm after 60 minutes. The reverse trend at the late stage might be caused by the aggregation of additives by themselves or caused by agglomeration of smaller particles connected by the

additive molecules. At high concentration, long polymeric chains might connect several small particles. The implication of size reversal is that there is an optimal concentration. In this work, the selection of the most effective additive and the optimal concentration is based on the vial test and particle sizing in diluted samples. We have also performed flow tests with 100% crude without *n*-heptane. There is consistency from this work and flow tests in tubes. In flow testing, the concentration of additives is with respect to the petroleum fluid. The optimal concentration in flow testing is in the range of 200 to 500 ppm. Results of flow testing will be submitted for publication shortly.



Fig. 1—Wax sedimentation in various vial tests of the mixture of 0.5-g petroleum fluid AG-1 and *n*-heptane $(1 \text{ g}:20 \text{ cm}^3)$ at 15°C: (a) at three different times with no additives; (b) at 48 hours without (left) and with 25-ppm B04 (right); (c) with 1,000-ppm A04, A05, and A06 (from left to right in each picture).



Fig. 2—Wax-particle-size distribution by DLS with A04 at different dosages in the mixture of AG-1 and n-heptane (1 g:10 cm³) at 20°C.

Polarized-light microscopy was used to examine the wax-particle sizes. Microscope images in **Figs. 4a and 4b** reveal that, without additives, plate-like particles are formed in the mixture of AG-1 and *n*-heptane in bright field and polarized light. The crystal size is approximately $50 \mu m$. Polarized-light microscopy provides higher resolution for such crystalline structures, as shown in Figs. 4b through 4f. Adding A04 can prevent the formation of large crystals. Figs. 4c and 4d illustrate the wax crystals from AG-1 and *n*-heptane mixtures at 100- and 500-ppm concentrations of A04, which consists of small-crystal particles. Particle size in Fig. 4d is smaller than in Fig. 4c, illustrating dependency on A04 concentration. By adding crystal modifier B04, even smaller crystals are observed (Figs. 4e and 4f). At higher concentration, smaller wax crystals are observed. No plate-like wax crystals are formed by adding A04 and B04, as shown in Figs. 4c through 4f.

The vial testing and DLS sizing presented previously are all performed in diluted petroleum fluids. Viscosity measurement without dilution is another approach in examining the effectiveness of the additives below the WAT. The comparison of viscosity between petroleum fluid AG-1 (blank) and AG-1 at 500-ppm A04 is presented in **Fig. 5a.** The measurements start at 50°C, at which temperature the samples are homogeneous with no wax crystallization. AG-1 oil has a viscosity of 2.97 cp at 50°C. By adding 500-ppm A04, the initial viscosity is 3.30 cp, 11% higher, because of the high molecular weight and structure of the polymer additive. The temperature

then decreases at the rate of 0.5° C/min. Viscosity increases as the temperature drops. The temperature at which the viscosity slope changes provides the WAT. As seen in the inset in Fig. 5a, the WAT of AG-1 is 44.5°C. With A04, the WAT is depressed marginally. Afterward, the viscosity of AG-1 with A04 increases at a slower rate to reach 19.1 cp at 5°C. In comparison, AG-1 has viscosity of 24.6 cp at 5°C, approximately 30% higher. The results demonstrate that the wax dispersant A04 can improve flowability. Such findings are consistent with the vial testing and particle sizing/imaging. Measurements at cooling rates of 1.0° C/min and 2.0° C/min were also conducted. No significant difference from 0.5° C/min was observed.



Fig. 3—Wax particle-size distribution by DLS with B04 at different dosages in the mixture of AG-1 and *n*-heptane (1 g:10 cm³) at 20°C.



Fig. 4—Microscope images of wax crystals of the mixture of AG-1 and *n*-heptane (1 g:10 cm³): (a) in bright field; (b) in polarized light; with (c) 100-ppm A04; (d) 500-ppm A04; (e) 25-ppm B04; (f) 200-ppm B04 at 15°C.



Fig. 5—The viscosity dependence of crude oils with additives on temperature. The temperature decreases from 50 to 5°C at a rate of 0.5°C/min. The inset charts in (a) and (b) enlarge the curves where WAT values are read.

The rheological properties of AG-1 with wax modifier B04 were also investigated, as presented in Fig. 5b. The initial viscosity values are close for the three samples, 2.97 cp for AG-1, 2.95 cp for AG-1 with 25-ppm B04, and 3.00 cp for AG-1 with 100-ppm B04. From the inset in Fig. 5b, the WAT is depressed from 44.5°C (blank) to 40.5°C at 25-ppm B04. When the dosage increases, the WAT stays in a narrow range between 38 and 40°C. As the temperature decreases, the viscosity of AG-1 mixed with B04 increases at a slower pace to reach 18.3 cp (25 ppm), 17.2 cp (50 ppm), 16.3 cp (100 ppm), 14.7 cp (200 ppm), 15.4 cp (300 ppm), and 15.7 cp (500 ppm) at 5°C. In comparison, AG-1 has a higher viscosity of 24.6 cp at 5°C. It is interesting to observe the reverse trend from 200 to 500 ppm. We witnessed the reversal in particle size in Figs. 2 and 3 in line with viscosity reversal.

Because B04 shows effectiveness in AG-1, the effect of B04 on rheological properties of AG-2 and AG-3 is also investigated. Fig. 5c presents the results of adding B04 to AG-2 at different dosages. AG-2 has a wax content close to that of AG-1, but it is a denser fluid. It has a viscosity of 70.0 cp at 5°C. Addition of 300-ppm B04 can reduce the viscosity by approximately 75% to 16.5 cp. We also observe the reversal of the trend from 300 to 500 ppm. Fig. 5d presents the results from AG-3, in which the effectiveness of B04 is less pronounced because of the lower wax content in AG-3. The optimal dosage is observed to be approximately 100 ppm, at which the viscosity is reduced from 20.3 to 14.2 cp.

From these rheological measurements, it is demonstrated that crystal modifier B04 has a higher effectiveness in reducing viscosity when the temperature drops below the WAT. The optimal dosage varies from 100 to 300 ppm, depending on the petroleum fluid. When the dosage is above the optimal value, the viscosity might increase, consistent with sizing measurements.

We have demonstrated that both wax dispersant (A04) and crystal modifier (B04) not only depress the WAT but also reduce crystal size and change crystal morphology. In **Fig. 6**, we provide a sketch to show the mechanism of crystal modifiers and dispersants. In the sketch, a crystal modifier is a comb-like polymer. The backbone chain cocrystallizes with the native paraffin waxes. The side chains are branched alkanes that do not participate in crystallization. These chains stay on the wax-crystal surface, and dissolve in the oil phase. They provide the steric repulsion among the wax particles. In this way, the crystal growth in every direction is restricted, and the size remains small. The dispersant in Fig. 6 is a polymer with phenol groups. The backbone chain can adsorb onto wax crystals and the pipe surface. The hydrophilic phenol groups might make the surface water-wet, thus minimizing the tendency of wax crystals to grow or to adsorb onto the pipe surface. To demonstrate the difference in the mechanisms of the two additives, we perform contact-angle measurements and examine the effect of a small amount of water on the wax-crystal particle size.

The contact angle of a 5%-NaCl (reservoir brine) droplet on stainless steel is measured to be $102.6 \pm 0.2^{\circ}$. After the steel is coated with A04, the contact angle deceases to $66.7 \pm 3.3^{\circ}$. In comparison, the contact angle remains at $101.4 \pm 0.4^{\circ}$ when the steel is coated with B04. Similar results are observed when deionized water is used instead of brine. The wax dispersant A04 is surface-active, which changes the stainless-steel surface to more water-wet.

A small amount of 5%-NaCl solution is added to AG-1/*n*-heptane mixture, and crystal sizes are measured by DLS. The results are presented in **Fig. 7.** In the reference test in AG-1 with no additive, the mean size is not appreciably affected by the brine; only the distribution becomes wider at 60 minutes. These changes may be caused by the native surface-active components in the petroleum fluid. In the test at 500-ppm A04, the mean size decreases from 670 to 480 nm at 60 minutes. The distribution also becomes narrower. Although the aqueous phase is separated before the oil phase is analyzed, there might be a thin layer of water on the wax-particle surface that might prevent or reduce the aggregation. In comparison, there is little change in the test in the mixture at 200-ppm B04. The results demonstrate that an aqueous phase can increase the performance of a dispersant, but there is little impact on the crystal-modifier effectiveness. We have found that the addition of a small amount of water increases the effectiveness of the dispersant in flow testing.



Fig. 6—Proposed mechanisms of paraffin-wax crystallization and mitigation by crystal modifiers and wax dispersants.



Fig. 7—Particle-size distribution at 10 and 60 minutes: (a) mixture of AG-1 and *n*-heptane (1 g:10 cm³), (b) with 500-ppm A04 and (c) with 200-ppm B04 with or without brine.

The effect of the aqueous phase on the crystals in the oil phase is also examined by microscope. Little difference is seen in the crystal size of the reference and B04 from the effect of brine. However, there are significant differences in crystal size with A04 in the presence and in the absence of brine, as shown in **Fig. 8**. When there is no brine, each bright particle consists of several small ones (see Fig. 8), indicating aggregation. In comparison, there is much less aggregation when there is a small amount of brine.



Fig. 8—Polarized-light microscope images of wax crystals of AG-1 with 500-ppm A04 (a) without brine and (b) with brine.

Conclusions

We have performed a systematic study of stabilization of wax-crystal particles in three waxy petroleum fluids. Numerous crystal modifiers and dispersants have been evaluated by vial testing for the three crudes. We selected the most effective additive from each group on the basis of sedimentation testing, and investigated wax-particle size, crystal morphology, and rheological properties. It is found that both additive types reduce wax-particle size and change crystal morphology. The dependence of viscosity on temperature during cooling from 50 to 5°C reveals that the additives can reduce the viscosity at lower temperatures. Water (brine) has a significant impact on the effectiveness of the dispersants, because of the alteration of surface wetting as wax particles become more water-wet. A small amount of water might prevent wax-particle growth. The strong surface effect is not observed in crystal modifiers. On the other hand, crystal modifiers are more effective in controlling wax-particle size and morphology. We observe a reversal in the effectiveness of both dispersants and crystal modifiers at high concentrations. The reversal might be caused by self-aggregation of additives or agglomeration of crystal particles being connected at a high concentration in the bulk.

The main motivation of this work relates to wax mitigation in oil and gas production. A reduction of the size of crystals might also find applications in storage tanks.

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Appendix A—Further Analysis of Wax Sedimentation

In Appendix A, we present the sedimentation of wax particles in the vials. Generally, below the WAT, the waxes are expected to form and segregate at the bottom of the vials. Viscosity data in Figs. 5a and 5b give a clear evidence of wax formation, as we discussed in the text. Initially, when we examined AG-1 in vials below WAT, we did not observe wax precipitation even after a few days. We attributed the lack of precipitation to the closeness of density between the wax particles and the background fluid. However, when we mixed the crude with *n*-heptane, wax precipitation was observed in a short time. Here, we use microscopy to examine wax particles along the vials for all three crudes. The work presented here is based on the same three petroleum fluids described in the text, but the samples experienced some evaporation during several months. We will provide relevant densities, which provide an indication of the loss of some lighter species compared with the fresh petroleum fluids used in the text. There should be no qualitative difference between fresh samples in the text and samples that have lost some volatile components. We start with sample AG-1. The density of this sample is 0.84 g/cm^3 at room temperature. We homogenize it by rigorous manual mixing in the original container, and then place the sample in 10-cm^3 Kimble-glass conical-bottom vials (length = 114 mm, outside diameter = 16 mm). After 7 days, there is no precipitation. A similar procedure was applied to AG-2 (density = 0.85 g/cm^3) and AG-3 (density = 0.85 g/cm^3). In AG-2, no wax precipitation was observed. In AG-3, however, wax precipitation was noticeable at the bottom of the vial around the walls. **Fig. A-1** shows these three samples after 7 days. We also take fluid samples from the top, the middle, and toward the bottom of each vial, and place them on glass slides under the microscope. **Fig. A-2** shows the particle images taken under polarized light by our Leica DM2700M microscope. As clearly seen, the sample from the vial top has very few wax crystals. The sample from the middle has a higher number of wax crystals, and the bottom sample has an even higher number of larger crystals. In AG-2, the concentration of wax particles is more pronounced at the bottom. In AG-3, wax particles are connected and have made larger crystals.



Fig. A-1—Wax sedimentation in vial tests for AG-1, AG-2, and AG-3 at 7 days. In AG-3, the sedimentation is on all walls to the dashed line.



Fig. A-2-Microscopic images of wax particles from the top, middle, and bottom of the vials depicted in Fig. A-1.

Wax-sedimentation vial tests with *n*-heptane were repeated to provide reproducibility with the results in the text. Two sets of experiments were performed: one in the same way as before by mixing 0.5 g oil and 10 cm^3 *n*-heptane (**Fig. A-3**) and the other by a higher amount of oil: 1 g oil in 10 cm^3 *n*-C₇ (**Fig. A-4**). The AG-1 sample was first heated to 50° C above the WAT, and then it was mixed with *n*-heptane in a 15-cm³ centrifuge tube at room temperature ($\approx 20^{\circ}$ C). The tubes were put on a rack after mixing, and the sedimentation behavior was monitored. As shown in Fig. A-3a, wax precipitation is observed at the bottom of the tube after 20 minutes, which increases over time. Adding only 25 ppm of B04 reduces paraffin-wax sedimentation compared with the reference case. Results are shown at 48 hours (Fig. A-3b). Fig. A-3c presents the results from adding dispersants A04, A05, and A06 at a concentration of 1,000 ppm at 2 and 60 minutes. Similarly, noticeable wax sediments are observed in all the three tubes after 60 minutes. However, the amount of sediments is less when A04 and A05 are added, than when A06 is added. Tests with a higher amount of oil (1 g) provide similar results. The wax deposition increases over time (Fig. A-4a). B04 reduces the wax sedimentation (Fig. A-4b).



Fig. A-3—Wax sedimentation in various vial tests of the mixture of 0.5 g of petroleum fluid AG-1 and *n*-heptane (10 cm^3) at 20°C: (a) at three different times with no additives; (b) at 48 hours without (left) and with 25-ppm B04 (right); (c) with 1,000-ppm A04, A05, A06 (from left to right) at 2 minutes and at 60 minutes.



Fig. A-4—Wax sedimentation in various vial tests of the mixture of 1 g of petroleum fluid AG-1 and *n*-heptane (10 cm³) at 20°C: (a) at three different times with no additives; (b) at 48 hours without (left) and with 25-ppm B04 (right); (c) with 1,000-ppm A04, A05, A06 (from left to right) at 2 minutes and at 60 minutes.

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