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Micromechanical Adhesion Force Measurements between Hydrate Particles in Hydrocarbon Oils and Their Modifications

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Cyclopentane (CyC5) hydrate interparticle adhesion force measurements in the presence of small amounts of crude oil (up to 8 wt % in cyclopentane) were performed at 3.2 °C, under atmospheric pressure, using a micromechanical force apparatus. The adhesion forces obtained for cyclopentane hydrate in small amounts of crude oil in CyC5 bulk fluid were lower than those measured for CyC5 hydrate in pure CyC5 bulk fluid. CyC5 hydrate-normalized adhesive forces were measured to be on the order of 0.5 mN/m for samples containing approximately 5–8 wt % of Caratinga and Troika crude. Hydrate-normalized adhesive forces were found to increase when the surface-active components (including acids and asphaltenes) were removed from the crude oil. These results suggest that crude oils with high contents of acids and asphaltenes may be more likely to exhibit nonplugging tendencies in oil and gas flowlines.

Introduction

Gas hydrates are solid, ice-like compounds that encapsulate small gas molecules, such as methane, ethane, and propane. These compounds are usually stable at low temperatures and high pressures (e.g., 298 K, 15 bar¹). Gas hydrates are commonly formed in offshore oil and gas flowlines, in some cases completely halting production. The formation of gas hydrates is a major flow assurance concern for the deepwater petroleum industry.²

In oil-dominated systems, hydrates are formed from water droplets emulsified in the oil phase. Once the water droplets are converted to hydrates, the agglomeration of hydrate particles is a critical step to forming hydrate plugs in oil and gas flowlines. Determining the adhesive forces between individual hydrate particles is important for characterizing the agglomeration behavior in flowlines. A micromechanical apparatus was developed to measure the adhesive forces between hydrate particles and to gain insight into the agglomeration tendencies of hydrates.³ Liquid hydrate formers, such as tetrahydrofuran (THF), ethylene oxide (EtO), and CyC5, are typically used as gas hydrate analogues when experiments are performed at atmospheric pressure, where these hydrate formers are stable at temperatures close to the ice point (0 °C). As determined in previous studies,⁴ CyC5 is a better model hydrate system for the micromechanical apparatus than the cyclic ether hydrates, THF and EtO; cyclic ether hydrate formers have high vapor pressures and quickly evaporate

during the course of the experiments. As a consequence of the evaporation of the cyclic ethers, the bulk fluid (stoichiometric mixture of cyclic ether and water) becomes water-rich and, at cold temperatures, ice may form.^{4,5} Additionally, CyC5 hydrate is a good model system because it allows for measurements to be taken above the ice point up to the hydrate equilibrium temperature of 7.7 °C (at atmospheric pressure)² and measurements may be performed in pure CyC5 bulk fluid. Moreover, CyC5 hydrate is a sII former (most pipeline hydrates are sII⁶) and is immiscible with water, similar to hydrophobic natural gas formers, such as methane and propane.

Several studies have been reported on the adhesion of particles, for both ice and hydrates, using micromechanical techniques. Hosler et al.⁷ and Fan et al.⁸ studied the adhesion of ice particles using micromechanical techniques. The CSM laboratory previously measured the interparticle adhesion forces between THF hydrate particles and ice particles (with diameters on the order of 500 μm).^{3,10} However, the quantitative results in this present paper may not be directly compared to those previous results, which were obtained using a higher preload force between hydrate particles. Taylor et al. found that, as the preload force increases, the measured adhesion force between hydrate particles also increases.¹⁰ It has been suggested that the measured hydrate forces could be best represented by the capillary bridge theory, where a quasi-liquid layer exists on the hydrate surface.^{3,4,10}

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Taylor performed the first CyC5 adhesion force measurement on the micromechanical force apparatus as a part of his hydrate adhesion scoping study,¹⁰ at a higher preload force than the results presented in this paper. He found that the CyC5-normalized adhesion forces were significantly lower than those of THF hydrate, which was attributed to the higher surface roughness that he observed with the CyC5 hydrate particles compared to the THF hydrate particles. CyC5 hydrate adhesion force measurements in pure CyC5 bulk fluid over a temperature range from 1 to 6 °C were presented elsewhere^{4,5} and serve as a base case for the crude oil hydrate interparticle adhesion force measurements.

In preliminary micromechanical force measurements of the normalized adhesion forces between CyC5 hydrate particles in approximately 3–5 wt % unmodified and deasphalted Troika crude oil at 3.5 °C, it was suggested that the asphaltene content in a crude oil may be in part responsible for lowering the adhesion forces of hydrate particles.⁵ This indicated that changes in the crude oil chemistry can affect the adhesion forces between hydrate particles, which, in turn, can impact the aggregation of hydrate particles that causes hydrate blockage in oil and gas pipelines.

The idea that the presence of asphaltenes at the hydrate surface increases the surface activity and may decrease the plugging tendency of a crude oil is supported by other studies by Buckley et al.,¹¹ Hemmingsen et al.,¹² and Fadnes et al.,¹³ although some opposition to this idea exists in the literature from Borgund et al.¹⁴ Resins and asphaltenes are considered surface-active components within the crude oil, and as a rule of thumb, the interfacial energy decreases with surface activity.¹⁵

Asphaltenes are defined as the components of crude oil that are soluble in aromatic species, such as toluene, and insoluble in paraffins, such as *n*-pentane.⁹ Asphaltenes are high-molecular-weight, hydrophobic, hydrocarbon structures with hydrophilic, polar functional groups, such as aldehydes, carbonyl groups, carboxylic acids, amines, and amides. The asphaltene fraction of the crude oil contains the majority of the nitrogen, sulfur, and oxygen atoms, typically referred to as the heteroatoms. Asphaltenes exist within the crude oil as suspensions of microcolloids of approximately 3 nm in diameter.^{15–17}

Similar to asphaltenes, resins are polar compounds containing heteroatoms but are less aromatic and have a slightly lower molecular weight. They are typically defined as the fraction of the crude oil soluble in pentane and heptane but insoluble in liquid propane. Resins adsorb onto the asphaltene

aggregates and disperse the asphaltenes within the crude oil.¹⁸ Naphthenic acids, which are one of the oil components removed in the pH-14 extraction process of crude oils, are typically considered resins.^{16,17}

The effect of acids on the plugging tendency of crude oils has been studied by Aspenes et al.¹⁹ and Borgund et al.¹⁴ Aspenes et al. found that the contact angle between water and a glass surface in the presence of petroleum ether bulk fluid increased with the addition of 0–5000 ppm of commercially available (Aldrich) naphthenic acids added to the petroleum ether bulk fluid. Specifically for the glass surface, the contact angle increased from 29° to 40°, which would suggest that, with the addition of acids, capillary forces decrease based on the capillary bridge theory.²⁰ Borgund et al.¹⁴ compared the degree of excess acids (difference between total acid number and total base number) as a function of the plugging tendency of the crude oil. In most cases, crude oils with more acids than bases were nonplugging oils. Because of the complexity of crude oil systems, comprised of thousands of components, it is difficult to isolate the contributions of individual components within a crude oil, which lead to its nonplugging tendency. However, recent work by Erstad et al.²¹ reported that the type of acid in a crude oil is more important for determination of a nonplugging crude oil than the amount of acids when determining whether a crude oil is plugging or nonplugging. Erstad et al.²¹ suggested that a crude oil with ester carbonyl components is less likely to plug.

This paper presents micromechanical adhesion force experiments on CyC5 hydrate particles in three crude oils and their modifications (deasphalted and pH-14 extracted) to understand the effect of asphaltenes and acids on the agglomeration properties of hydrate particles. This work is important in providing further insight into the role of surface-active components of crude oils in the prevention/remediation of hydrate plugs in oil-dominated subsea pipelines.

Materials and Methods

The second-generation micromechanical force apparatus used in this study improved the accuracy and repeatability in measuring the forces between hydrate particles.¹⁰ The micromechanical apparatus consisted of an inverted light Carl Zeiss Axiovert S100 microscope equipped with a digital recording system. The glass fiber cantilevers were located within an aluminum cooling cell. The left glass fiber cantilever was positioned within the viewing area of the microscope and remained stationary during the experiment. The right glass fiber cantilever was connected to a high precision, remote-operated Eppendorf Patchman 5173 micromanipulator. Additional details about the micromechanical force apparatus may be found elsewhere.²²

A schematic of the cantilever movements inside the cell is shown in Figure 1. The displacement of the hydrate particles was

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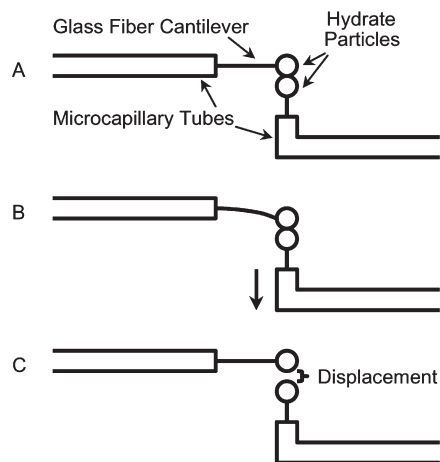


Figure 1. Schematic of the micromechanical apparatus experimental technique. (A) Particles are brought into contact at a known preload force. (B) Particles are slowly pulled apart. (C) Particles have separated. The displacement is measured to determine the adhesion force. Adapted from Taylor et al.¹⁰

captured by digital video microscopy and analyzed using the computer program Image J.²³ The remote-operated manipulator was used to apply a hydrate particle preload force of approximately 0.7 N. After contact, the particles were slowly pulled apart until, at some critical displacement, the particles broke apart.

The adhesion force (F) between the hydrate particles was determined using Hooke's law, where the force between the particles is directly proportional to the spring constant (k) of the glass fiber cantilever and the displacement of the particles (x).

$$F = kx \quad (1)$$

The spring constant of the stationary cantilever was indirectly calibrated using a tungsten wire of known spring constant. The tungsten wire was directly calibrated using a Denver Instruments TB-215-D analytical laboratory scale. The calibration methods have been thoroughly explained by Taylor.²²

A total of 40 pull-off measurements were performed for each experiment to obtain an adhesion force distribution. The average of the 40 measurements is presented on all of the adhesion force charts, with the bars (vertical lines) representing the standard deviation of the 40 measurements. Each force measurement was normalized by the harmonic mean radius (R^*) of the particle pair, defined as

$$\frac{1}{R^*} = \frac{1}{2} \left[\frac{1}{R_1} + \frac{1}{R_2} \right] \quad (2)$$

where R_1 and R_2 are the radii for particles one and two. In the capillary bridge theory²⁰ mechanism for hydrates, a liquid is expected to wet the hydrate particle surfaces. When the particles come into contact, the liquid forms a bridge between the particles, and the attraction between the particles is caused by a Laplace pressure. The maximum attractive force between two smooth, spherical particles because of capillary bridging is described by

$$\frac{F_{\text{CBT}}}{R^*} = 2\pi\gamma_{\text{LL}} \cos \theta \quad (3)$$

where γ_{LL} is the liquid–liquid interfacial energy, θ is the liquid contact angle on the solid particle, and R^* is the harmonic mean radius of the particle pair. While the capillary bridge theory (assuming a contact angle of 0° because of the

hydrophilic nature of the hydrate surface) overpredicted the maximum hydrate adhesion forces, the model was shown to match the qualitative trend that the hydrate adhesion force increases with increasing interfacial energy. This overprediction was expected because of the surface roughness of the hydrate particles,²⁴ as observed during the adhesion experiments. Israelachvili²⁰ suggests that asperities as small as $1\text{--}2\ \mu\text{m}$ can significantly lower the measured adhesion from the capillary bridge theory. The capillary bridge theory has also been used to explain the temperature dependence of the adhesive forces, where with increasing temperature, an increase in the quasi-liquid layer would reduce the effects of hydrate surface roughness by filling in the surface asperities with liquid, increasing the contact area between the hydrate particles.²²

CyC5 hydrate adhesion force measurements were performed in the presence of small weight percents of three different crude oils in the CyC5 bulk fluid. To form the CyC5 hydrate particles, a quenching method was used. A dropper was used to place a drop of deionized water on the end of one of the glass fiber cantilevers. Immediately afterward, the droplet was quenched in liquid nitrogen. Then, the glass fiber cantilever was placed inside the aluminum cooling cell containing pure CyC5 liquid (99% pure, Sigma Aldrich). This method was repeated for the other glass fiber cantilever. The cell temperature was then raised above the ice point to provide a driving force for hydrate formation. It is important to note that the experimental temperature was raised above the ice formation temperature to eliminate the possibility of ice existing as a second phase within the hydrate particle. Then, the desired amount of crude oil was mixed into the existing CyC5 liquid within the cell. Because of the visibility limitations of the micromechanical apparatus, the bulk fluid mixtures could not exceed 8 wt % for any of the crude oils studied. As a result of the visibility limitation and the high relative volatility of CyC5 when compared to the crude oils studied, a gas saturation system was added to the micromechanical apparatus. This system prevented excessive CyC5 evaporation by bubbling nitrogen gas through CyC5 liquid before entering the experimental chamber. This new addition mitigated the evaporation of CyC5.

Ice-normalized adhesion force measurements were performed to compare the results obtained for the hydrate-normalized adhesion force measurements. The ice particles were formed by quenching a water droplet on the end of each glass fiber cantilever. For the micromechanical experiment, the ice particles were placed in a saturated water-in-decane solution below 0°C .

The crude oils were modified by deasphalting and pH-14 extraction processes performed by the Norwegian University of Science and Technology (NTNU). Bulk properties for all unmodified and modified crude oils used in this study are available elsewhere.⁵ For the deasphalting process, the asphaltenes were precipitated out of the crude oil using excess *n*-pentane. The asphaltenes were then filtered through a $0.45\ \mu\text{m}$ filter, and the *n*-pentane was distilled off from the crude oil. For the pH-14 extraction process, the acidic components were extracted with a 30:70 water/ethanol solution, where sodium hydroxide was used to obtain the final pH; this process was repeated 10 times. These modifications were made to study the effect of individual classes of components of the oils, specifically the asphaltenes and acids, on the hydrate interparticle adhesion force measurements. One important consideration regarding these modified crude oils is that, while the deasphalting and pH-14 extraction processes do chemically remove the desired components (asphaltenes and acids, respectively), the magnitude of which these processes affect other aspects of the crude is not well-defined. A substantial

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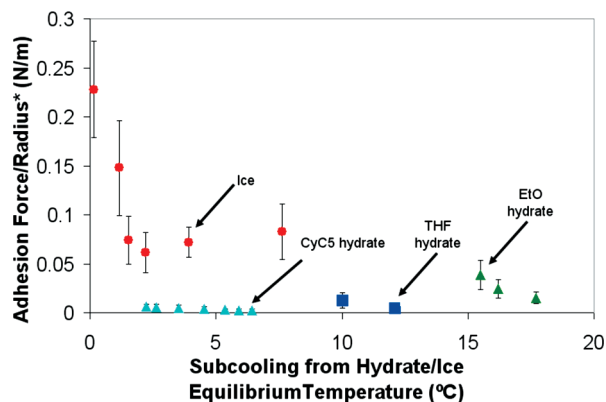


Figure 2. CyC5, EtO, and THF hydrates adhesion force measurements compared to ice as a function of subcooling from their respective equilibrium temperatures of 7.7, 11.1, and 4.4 °C.

amount of time has been devoted to characterizing the individual chemical components within a crude oil, which reduce its plugging tendency.^{12–14,21,25} The oil modifications tested in this study (pH-14 extracted and deasphalted) qualitatively indicate how the asphaltenic and acidic fractions of crude oil impact agglomeration. Actual values for the adhesion force and interfacial tension for unmodified Caratinga and Troika oils should not be assumed to be representative of a general crude oil.

Results and Discussion

Ice Adhesion Forces. Figure 2 shows the normalized interparticle adhesion forces for ice particles in a saturated water-in-decane continuous phase as a function of subcooling; these are compared to the previously characterized CyC5 hydrate, THF hydrate, and EtO hydrate interparticle adhesion measurements.⁵ Each data point represents the average of 40 pull-off adhesion force measurements, and the bars represent the standard deviation between the 40 pull-off adhesion force measurements. The results show that the normalized adhesion forces for the ice system (where the continuous phase is saturated with water) were higher than all of the hydrate-normalized adhesion forces studied. Also, even though THF and EtO hydrate-normalized adhesion force results were obtained at higher subcooling than CyC5 hydrate, the adhesion forces for the cyclic ether hydrates were between the adhesion forces of ice and CyC5 hydrate systems. The normalized adhesion force for CyC5 hydrate at 5 °C subcooling was measured to be more than 80% lower than those obtained for the cyclic ether hydrates, THF and EtO, at 10 and 15 °C subcooling, respectively.

Crude Oil Adhesion Force Results. The micromechanical adhesion force measurements of cyclopentane hydrate in the presence of small weight percents of Caratinga, Troika, and Dalia crude oils and their modifications at 3.2 °C are summarized in Figures 3–5. Also, a line is added on each figure to show the base case of CyC5 hydrate in pure CyC5 liquid at 3.2 °C.⁵ The fit lines were added to guide the eye and qualitatively describe data trends.

Variability between the hydrate adhesion force pull-off measurements is expected, as represented by the bars (dotted lines) on each data point (standard deviation between the

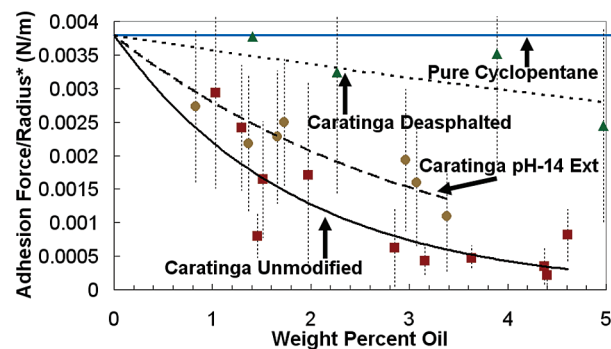


Figure 3. Summary of adhesion results in unmodified (■), deasphalted (▲), and pH-14 extracted (●) oils for Caratinga crude oil.

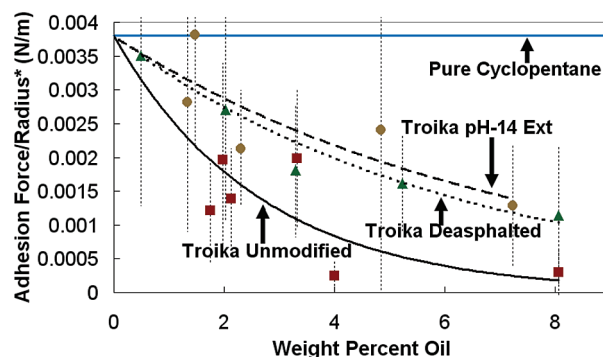


Figure 4. Summary of adhesion results in unmodified (■), deasphalted (▲), and pH-14 extracted (●) oils for Troika crude oil.

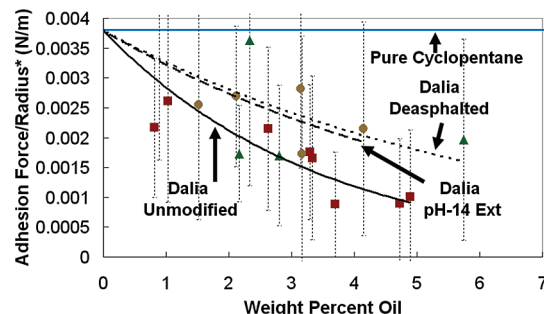


Figure 5. Summary of adhesion results in unmodified (■), deasphalted (▲), and pH-14 extracted (●) oils for Dalia crude oil.

40 pull-off measurements). Because CyC5 hydrate particles are known to have surface roughness,²⁴ slightly different alignment of the particles will unavoidably have differing contact areas, leading to a distribution in the force measurements. The differing contact areas, with the addition of small amounts of a complex fluid, such as a crude oil, which is comprised of thousands of components, would only be expected to increase this distribution. This is especially important when considering that, at the low temperatures required to stabilize the CyC5 hydrates for these experiments, the cell temperature is likely below the wax appearance temperature for the crude oils. Kok et al.²⁶ tested the wax appearance temperature of 15 crude oils, with the lowest measured at 17 °C.

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Because micromechanical adhesion force measurements are designed to measure the adhesive properties of hydrates under no shear conditions, they do not completely describe the plugging tendency of a crude oil. If the system is highly sheared, although the hydrate interparticle adhesive forces may be relatively large, the hydrate agglomerates may break apart. Conversely, in the case of shut-in conditions in flowlines, the adhesive properties of even weakly agglomerating hydrate formers may become significant. Under typical oil pipeline flow rates, a combination of adhesion force and shear rate, along with the emulsion properties of a system, is expected to dictate the hydrate plugging tendency of crude oils.

Effect of Asphaltenes and Acids. The pH-14 extraction process was performed on the crude oils to understand the effect of acids on the plugging properties of the crude oils. The pH-14 extraction of the crude oils removed the acidic fraction at pH-14. Typically, this process is expected to remove polar acid groups, including naphthenic acids.²⁷ This method increases the interfacial energy and the precipitated asphaltenes within the crude oil (thus increasing the emulsion stability).⁵ It was found that removing the acids and asphaltenes from the crude oils clearly increased the adhesion forces measured for both Caratinga and Troika crude oils (Figures 3 and 4). This result matches the expected trend for the normalized adhesive forces (for pH-14 extracted modified oils) from the capillary bridge theory (eq 3), because acid removal increases both the interfacial energy of the crude oil and, by association, the normalized adhesive forces. The interfacial energy of all three deasphalted crude oils did not deviate more than 3 mN/m from their unmodified counterparts; the change in interfacial energy alone may therefore not be significant enough to alter the adhesion properties of the hydrate particles. However, asphaltenes are known to act as stabilizers for emulsions, and when they are removed, the wetting properties of the hydrate particles may change, thus altering the contact angle between the wetting fluid and the hydrate particles and increasing the adhesion between the hydrate particles.

The Dalia crude-oil-normalized adhesion forces for the modified and unmodified oil did not seem significantly different from one another (Figure 5). These results for the Dalia crude oils could be due to the relatively low asphaltene content (1.7%) when compared to the other crude oils (Caratinga, 6.2%; Troika, 3.3%). The relatively low asphaltene content of this oil might be readily dispersed by the available resins, even after the pH-14 extraction process, which would negate variations in the adhesive force. To fully understand the adhesive tendencies of crude oil, significant maturity must first be reached in understanding the microscopic, chemical interactions of its many components.

Effect of Interfacial Energy. The interfacial energy between the crude oil and water is typically considered a measure of the surface-active components present. With an increase in polar components and asphaltenes, a resulting decrease in interfacial energy is expected. As the interfacial energy of a system decreases, the capillary bridge theory (eq 3) suggests that the normalized adhesion force should decrease. The hydrate surface is assumed to be completely covered by a water layer; this assumption

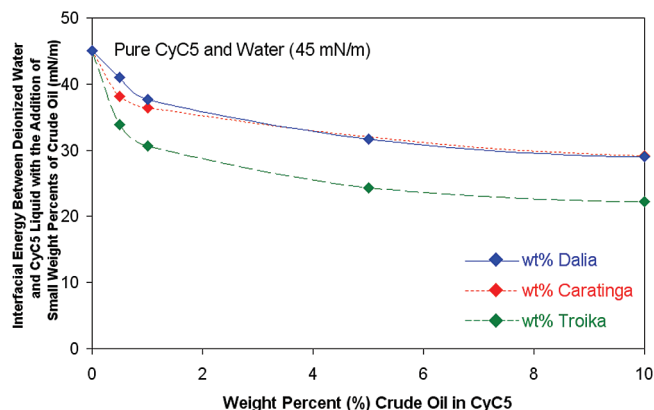


Figure 6. Interfacial energy plotted as a function of weight percent crude oil in cyclopentane.

predicts a contact angle of 0° , where the $\cos \theta$ term of eq 3 goes to unity.

With the addition of small amounts of crude oil into the CyC5 bulk fluid, a gradual decrease in the interfacial energy between the water and the original crude oils has been measured.²⁸ Hydrate-normalized interparticle adhesion forces of approximately 0.5 mN/m for unmodified Caratinga and Troika crude oils (at their highest weight percent oil measured) were obtained (Figures 3 and 4). The interfacial energy of the crude oils in CyC5 and water quickly decreases (with the addition of < 10 wt % oil) to its final value (100% oil; Figure 6). This suggests that the interfacial activity approaches its final value with the addition of 10 wt % oil and that the 0.5 mN/m adhesive force value is expected to be a reasonable value for the normalized CyC5 hydrate adhesion forces in pure crude oil systems.

Dalia crude oil measurements were obtained up to 5 wt % oil in CyC5 bulk fluid. However, the Dalia crude oil results did not seem to approach the same asymptotic value of the other two oils. Therefore, it is expected that, if additional Dalia crude oil experiments were to be performed at a higher weight percent crude oil in CyC5, the Dalia crude-oil-normalized adhesion force results would decrease further to a constant value. The interfacial energy data support the qualitative trend seen in the measured CyC5 hydrate adhesion forces; as the weight percent of crude oil in the CyC5 bulk fluid increases, a gradual decrease in the normalized adhesion forces for all of the oils and their modifications is observed (Figure 6).

Summary

The interparticle adhesion forces obtained for CyC5 hydrate in small amounts of crude oil in CyC5 bulk fluid were lower than those measured for CyC5 hydrate in pure CyC5 bulk fluid. CyC5 hydrate-normalized interparticle adhesive forces were measured to be on the order of 0.5 mN/m with samples containing approximately 5–8 wt % Caratinga and Troika crude oils (the highest crude oil weight percents measured). Hydrate-normalized adhesive forces were found to increase when the acids and asphaltenes were removed from the Caratinga and Troika

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crude oils. Dalia crude oil adhesion forces were not significantly different for the unmodified and modified derivatives; however, this may be attributed to its relatively low asphaltene content when compared to the other crude oils. These results are consistent with the findings that the Caratinga and Troika crude oils are considered

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nonplugging oils, while the Dalia is a plugging oil.²⁹ The CyC5 hydrate adhesion force measurements in crude oils suggest that crude oils with high contents of acids and asphaltenes may be more likely to exhibit nonplugging tendencies.

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