

## Paper II

Wettability of freon hydrates in crude oil/brine emulsions: the effect of chemical additives.



## WETTABILITY OF FREON HYDRATES IN CRUDE OIL/BRINE EMULSIONS: THE EFFECTS OF CHEMICAL ADDITIVES

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### ABSTRACT

In a previous work it was demonstrated that the wettability of freon hydrates generated in crude oil/brine emulsions can be evaluated from observation of changes in the point of phase inversion. The hydrates were categorized as oil wet, intermediate wet or water wet. The formation of oil wet hydrates was attributed to adsorption of specific molecular structures indigenous to some oils, i.e. natural hydrate inhibiting components. It was further found that the generation of oil wet hydrates could be correlated to low hydrate plugging tendencies at realistic conditions. In this work, the effect of chemical additives to oils that initially generate water- or intermediate wet hydrates is presented. Two biosurfactant structures and four naphthenic acid fractions extracted from crude oils have been added to crude oil/brine systems at low concentrations (ppm level). A significant effect on emulsion phase behaviour is observed, attributed to hydrate wetting alteration towards more oil wet behaviour from the adsorption of additives to the hydrate surfaces. It is found that the wetting alteration is crucially dependent on the crude oil/brine system in which the additives are tested. The findings are compared to hydrate plugging experiments at realistic conditions, showing that the correspondence between the hydrate wettability in freon systems and plugging tendencies of natural gas hydrates is dependent on the oil/brine interfacial tension of the system.

*Keywords:* hydrate, wettability, emulsion, inhibition, interfacial tension

### NOMENCLATURE

$\varphi_w^{inv}$  Point of phase inversion  
 $\varphi_w^0$  Point of phase inversion (no hydrates)  
 $\Delta\varphi_w^{inv}$  Difference in points of phase inversion with and without hydrates ( $\varphi_w^{inv} - \varphi_w^0$ )  
 $\Delta\varphi^*$  Differences normalised according to Eq. 1  
 $\Delta\varphi_{max}$  Maximum possible increase or decrease of  $\varphi_w^0$

### INTRODUCTION

In mixtures of gas and water, gas hydrates may form at certain temperature and pressure conditions. This work addresses the formation of hydrates in petroleum production. Once formed, the gas hydrates may be dispersed as particles and be transported with the fluid, or they may agglomerate into large hydrate clusters that can ultimately plug pipelines and platform equipment. It has been observed that while some crude oil systems have high risks of hydrate plugging, others have low or no tendency to form hydrate plugs at comparable condi-

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tions. The hydrate morphology is believed to be connected to the presence or absence of natural inhibiting components (NICs), as previously indicated by several authors [1, 2, 3, 4].

The surface energy of petroleum hydrates is believed to be a key parameter with regard to hydrate morphology and plugging tendency in petroleum production. At present, the surface energy of natural gas hydrates is unknown, but will depend on the fluids in which they grow. The wettability of the hydrates is governed by the surface energy, and will similarly be influenced by the properties of the fluids.

In a previous study [4] we demonstrated that crude oils generate hydrate particles of different wettabilities, varying from water wet to oil wet, depending on crude oil composition. The method is based on two aspects: a) Crude oil components adsorb to the hydrate surface, creating particles of varying wettability depending on crude oil composition, and b) these particles act as stabilizing colloidal particles in crude oil emulsions, and thus their wettability governs the emulsion behaviour. The experimental technique is based on observation of points of phase inversion in crude oil/brine emulsions, with and without hydrate particles. In an emulsion containing colloidal solid particles, one of the liquids is likely to wet the solid more than the other liquid, with the more poorly wetting liquid becoming the dispersed phase [5]. Hence, the type and stability of emulsions stabilized by colloidal particles are governed by the wettability of the solid. The effect of particle wettability upon emulsion behaviour has previously been a subject to several review papers [6, 7, 8, 9, 10]. A schematic illustration of spherical particles at a planar oil-water interface is given in Figure 1. The contact angles are by convention measured through the aqueous phase. Oil wet particles tend to stabilise water-in-oil emulsions, while water wet particles tend to stabilise oil-in-water emulsions. Several authors, e.g. Binks and Lumsdon [11, 12], have demonstrated that inversion of emulsions stabilized by solid particles, i.e. the shift from water-continuous to oil-continuous emulsions or vice versa, can be induced by altering the volume ratio of the two liquid phases. The point of phase inversion is dependent on the wettability of the solid particles.

In our previous study [4], hydrate wettabilities obtained from observing emulsion phase transition were compared to natural gas hydrate plugging ten-

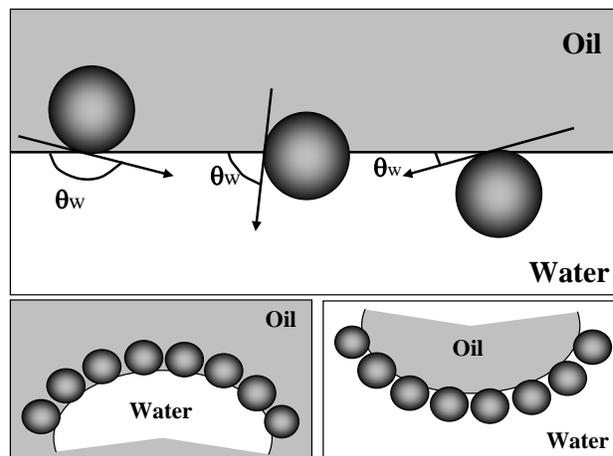


Figure 1: Spherical particles at planar oil/water interface. Oil-wet particles (contact angle  $> 90^\circ$ ) will reside mainly in the oil phase (right), and tend to stabilize water-in-oil emulsions. Water-wet particles (contact angle  $< 90^\circ$ ) reside mainly in the water phase (left), and tend to stabilize oil-in-water emulsions. (Adapted from Binks [7]).

dencies at realistic conditions. The results revealed that crude oils generating oil wet hydrates form hydrate dispersions, whereas crude oils generating intermediate wet or water wet hydrates form hydrate plugs. Hence, the presence of NICs prevent hydrate agglomeration through the formation of oil wet hydrates, a consequence of adsorption of NICs on the hydrate surfaces.

In the present work, chemical additives at low concentrations have been introduced to the crude oil/brine emulsions in an attempt to modify initially intermediate wet and water wet hydrate surfaces to an oil wet state. Both water soluble and oil soluble additives have been tested, and the effects are compared to their respective initial crude oil systems without additives. The results from some of the tests have also been compared to results from plugging tests at realistic conditions.

The chemical additives in this study are not arbitrarily chosen. We have previously indicated a link between the presence of NICs and the biodegradation level of the crude oils (i.e. the degree of microbial activity to which the crude oil has been exposed)[4]. Two biosurfactant structures, both products from microbial activity in oil, are therefore included in this work. Petroleum acids represent an interesting compound class that also is strongly connected to biodegradation [13]. Hence, naphthenic acids ex-

tracted from crude oils have been included in the study.

## MATERIALS AND METHODS

### Materials

#### Basic systems

The additives have been tested in four different crude oils from the Norwegian continental shelf, all of which have previously been found to generate water wet or intermediate wet hydrates [4]. The oils are labeled S-oils (sweet, non-biodegraded), and are assigned a digit and a letter according to field and well number.

Two aqueous phases have been tested. Most experiments were done using brine (3.5 wt% NaCl in double distilled deionised water), but some experiments using synthetic formation water (sfw) matching the S2b production stream were also performed.

Freon (R11), CCl<sub>3</sub>F, is used as the hydrate forming compound. This compound has a boiling point of 23.8°C and a low solubility in water (0.124g/100ml). The molecules form structure II hydrates below 8.5°C at 1 bar [14].

#### Water soluble additives

The molecular structures of the water soluble additives tested are given in Figure 2. HPMC (Hydroxy Propyl Methyl Cellulose), supplied by Sigma, has an average molecular weight of 86 000 g/mol. Surfactin and rhamnolipid are both biosurfactants, i.e. produced by microbial activity. Surfactin is a cyclic biosurfactant of the lipopeptide type with amino acids and hydroxy fatty acids incorporated in the structure. This compound was supplied by Sigma. Rhamnolipids are biosurfactants of the glycolipid type with carbohydrates in combination with long chain aliphatic acids or hydroxy aliphatic acids in the molecular structure. A sample of 25% rhamnolipids in water was received from Dr. I.M. Banat at the University of Ulster, Northern Ireland. Due to poor solubility of rhamnolipid in synthetic formation water, approximately 400 ppm of a commercial, non-ionic co-surfactant (Berol 160) was added to the formation water.

#### Oil soluble additives

The compounds used as additives to the oil phase are naphthenic acids extracted from crude oils. The

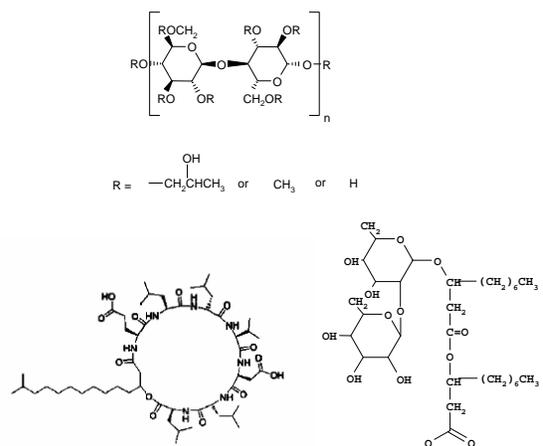


Figure 2: Molecular structures of the compounds tested as additives to aqueous phase. Upper: HPMC, Low left: Surfactin, Low Right: Rhamnolipid.

acids were extracted from the oils with an alkali solution, and back-extracted after a subsequent acidification of the aqueous extract with a mineral acid. A detailed description of the procedure is given elsewhere [13, 15, 16].

Petroleum acids were extracted from three biodegraded crude oils (B-acids), as well as from an acidic oil fraction received from the Mongstad oil refinery (M-acids). The petroleum acids were added in the concentration of 6.500ppm. In addition, the M-acids were tested at twice this concentration.

### Experimental methods

All emulsion tests were performed at 0°C.

The method for evaluating hydrate wettability from phase inversion in crude oil/brine emulsions was recently described in Høiland et al. [4]. The basic principle of the method is to determine the *point of phase inversion*,  $\phi_w^{inv}$ , i.e. the brine volume at which phase transition from oil continuous to water continuous emulsion can be observed when the brine to oil ratio is stepwise increased from 0.1 (i.e. 10wt% brine, 90wt% oil) to 0.9 (90wt% brine, 10wt% oil). The point of phase inversion is usually easily detected by an abrupt change in emulsion behaviour, e.g. the viscosity.

Since several compound classes indigenous to crude oil (e.g. asphaltenes, resins and naphthenic acids) are known to affect the properties of crude oil/brine emulsions [17], the points of phase inversion is de-

terminated for crude oil/brine emulsions both with hydrates ( $\phi_w^{inv}$ ) and without hydrate particles ( $\phi_w^0$ ) in order to elucidate the effect of the hydrates. The difference between the two inversion points is given as  $\Delta\phi_w^{inv}$ . The value of  $\Delta\phi_w^{inv}$  is correlated to the wettability of the hydrates present in each system, based on the fact that water wet particles will decrease the stability of the water-in-oil (w/o) emulsion whereas oil wet particles increase the stability of water-in-oil (w/o) emulsions (see above). Hence, a significant positive value of  $\Delta\phi_w^{inv}$ , typically larger than 0.1, indicate the presence of oil wet particles, whereas a significant negative value, typically less than -0.1, indicate the presence of water wet particles. In between are the intermediate wet, weakly oil wet and weakly water wet regimes.

The value of  $\phi_w^0$ , i.e. the initial inversion point for systems without hydrates, affects the maximum possible alteration of  $\phi_w^{inv}$  (decrease or increase) that hydrates may impose in either direction. In order to account for the influence of  $\phi_w^0$ , the values of  $\Delta\phi_w^{inv}$  are normalised according to Equation 1 [4]. Hence  $\Delta\phi^*$  is a number between -1 and 1.

$$\Delta\phi^* = \frac{\Delta\phi_w^{inv}}{\Delta\phi_{max}} \quad \begin{array}{l} \Delta\phi_w^{inv} > 0 \Rightarrow \Delta\phi_{max} = 1 - \phi_w^0 \\ \Delta\phi_w^{inv} < 0 \Rightarrow \Delta\phi_{max} = \phi_w^0 \end{array} \quad (1)$$

### Plugging tendencies of the crude oils

The plugging tendency, or morphology, of natural gas hydrates was tested in a high pressure sapphire cell from Sanchez Technologies. This equipment allows measurements at pressures up to 500 bar and temperatures down to -40 °C, making visual observation in a 40 ml volume possible. The experimental setup is described in detail by Fadnes [1]. The cell was initially loaded with water, and oil was added at elevated temperature, typically 70 °C, to give a watercut of 20 % by volume. A 750 rpm stirring rate was applied. Isobaric temperature sweeps were done, using a cooling rate of -5 °C, and a heating rate of +1 °C. The plugging tendencies of the systems were evaluated by visual inspection. The setup allow only a crude classification of the oils: dispersive, plugging. A dispersive system is one where all hydrates are present as a dispersion. A plugging system is one where the hydrates form aggregates. In

Table 1: Characteristics of crude oil systems used for tests of plugging tendencies. Brine is 3.5 % NaCl solution, and sfw is a synthetic formation water matching the S2b production stream.

Oil	GOR [Sm <sup>3</sup> /Sm <sup>3</sup> ]	Water	P [bar]	T <sub>eq</sub> [°C]
S2b	73	brine	100	14.8
S2b	73	sfw	100	14.5
S7b	61	brine	125	15.8
S7b	61	sfw	125	15.5

this context no attempt is made to differentiate between degrees of aggressiveness on agglomeration. Tests were performed for two of the oils used in the inversion point tests, using either 3.5 % NaCl solution, or synthetic formation water. Oil S2b was available as a pressurized separator fluid, while oil S7b was available as a stock tank oil, which was pressurized using a standard rich gas mixture. The GOR and the hydrate equilibrium temperature at the experimental pressure is given in Table 1 for each test system.

## RESULTS AND DISCUSSION

The initial inversion points for the crude oil/brine systems without additives are given in the upper pane of Figure 3. The values of  $\Delta\phi_w^{inv}$  in the lower left pane show that the presence of hydrates has little impact on the point of inversion compared to systems without hydrates. The hydrates generated in the crude oils S2b and S3a are slightly water wet (negative  $\Delta\phi_w^{inv}$ ), whereas intermediate wet hydrates are generated in crude oils S7a and S7b ( $\Delta\phi_w^{inv}$  equal to 0). The values of  $\Delta\phi_w^{inv}$  normalised according to Equation 1 is given in the lower right pane.

### The effect of the water soluble additives

The results from using 500ppm HPMC as chemical additive to the crude oil/brine systems are given in Figure 4. Apparently, the effect of HPMC on the emulsion phase behaviour is highly dependent on the crude oil/brine system in which it is tested. In most cases, the addition of HPMC significantly alter the inversion behaviour of the emulsions compared to the original emulsions without additives (given in Figure 3). This indicates an alteration of the wettability of the hydrate particles generated in

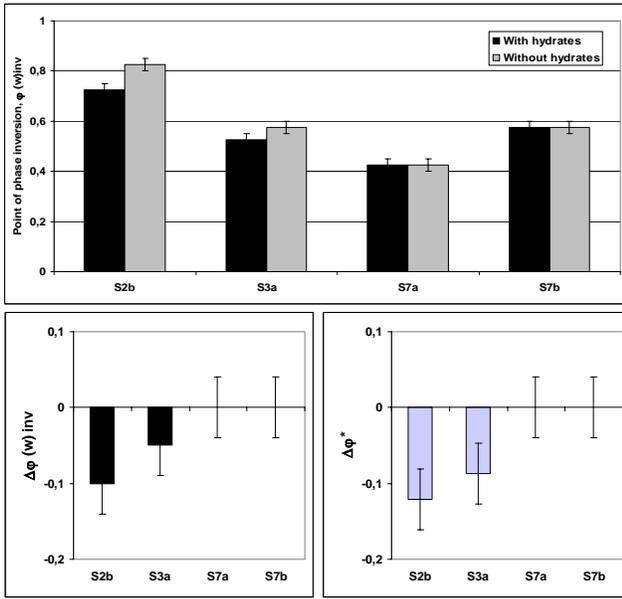


Figure 3: Upper:  $\phi_w^{inv}$  for systems without chemical additives. With (black) and without (grey) hydrates. Low left: Difference in  $\phi_w^{inv}$  for systems with and without hydrates. Low right: Normalized differences,  $\Delta\phi^*$ , with and without hydrates (no chemical additives), i.e. related to the initial inversion points of the systems without hydrates,  $\phi_w^0$ , as given by Equation 1. Data for S2b, S3a and S7a from Høiland et al. [4].

the modified systems compared to their initial state without HPMC present. For all systems except the S7b system the values of  $\Delta\phi^*$  are increased from their initial values given in Figure 3, indicating a wetting alteration of the hydrate particles from water wet (S2b and S3a) and intermediate wet (S7a) towards oil wet behaviour. The effect is most significant for the two initial water wet systems (S2a and S3a). For the S7b system a slight decrease in the  $\Delta\phi^*$  value is observed, but the effect is small and probably within the experimental error. Hence, a negligible shift in hydrate wettability on the addition of HPMC is observed for this system.

The effect of surfactin is given in Figure 5. The  $\Delta\phi^*$  value is slightly increased for the S3a system and slightly decreased for the S7b system compared to the initial states, i.e. without chemical additives (given in Figure 3). However, considering the experimental error, the effects of 10ppm surfactin on these systems are regarded as negligible.

Four different rhamnolipid systems have been investigated, three systems containing 500ppm rhamnolipids in the aqueous phase (two being 3.5wt%

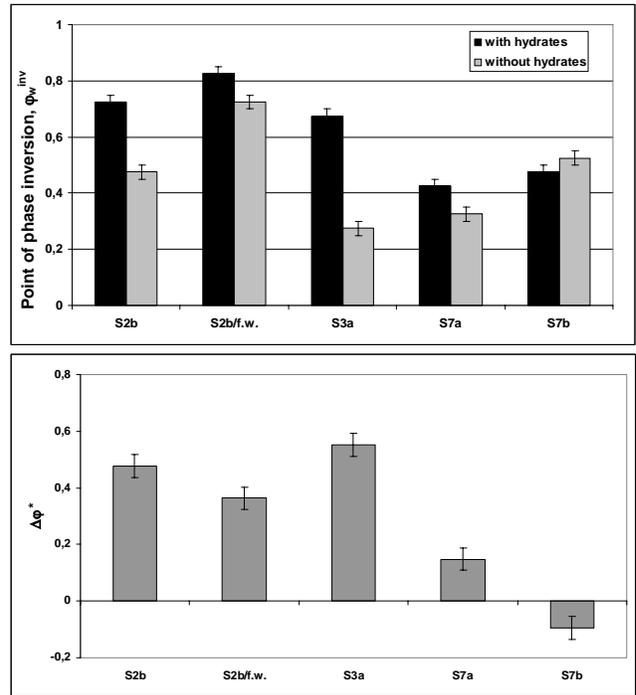


Figure 4: Upper:  $\phi_w^{inv}$  for systems with 500ppm HPMC in the aqueous phases (3.5wt% NaCl(aq) or synthetic formation water (f.w.)). With hydrates (black), without hydrates (grey). Lower: Differences in  $\phi_w^{inv}$  with and without hydrates, normalised according to Eq. 1.

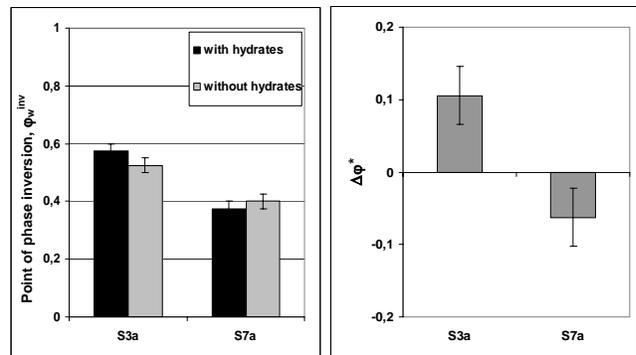


Figure 5: Left:  $\phi_w^{inv}$  for systems with 10ppm surfactin in 3.5wt% NaCl(aq). With hydrates (black), without hydrates (grey). Right: Differences in  $\phi_w^{inv}$  with and without hydrate particles, normalised according to Eq. 1.

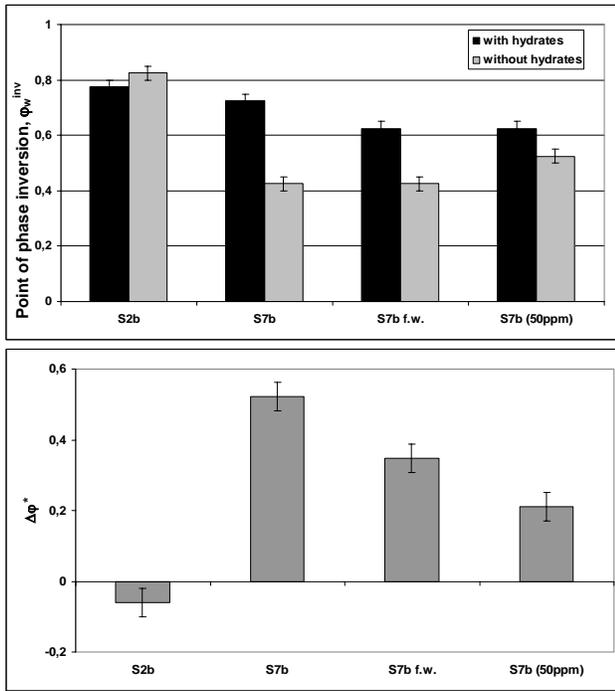


Figure 6: Upper:  $\phi_w^{inv}$  for systems with 500ppm or 50ppm (S7b) rhamnolipids in the aqueous phases (3.5wt% NaCl(aq) or synthetic formation water (f.w.)). With hydrates (black), without hydrates (grey). Lower: Differences in  $\phi_w^{inv}$  with and without hydrates, normalised according to Eq. 1.

NaCl(aq) and one being synthetic formation water containing 400ppm Berol 160), and one system containing 50ppm rhamnolipids in NaCl-brine. The results are given in Figure 6. Similar to the HPMC systems (Figure 4), the effect of the rhamnolipids strongly depends on the specific crude oil/brine system being investigated. For the S7b oil,  $\Delta\phi^*$  is significantly increased both at 500ppm and 50ppm compared to the original value of this oil (given in Figure 3). This indicates a wetting alteration from initial intermediate wet hydrates towards oil wet hydrates. The effect of rhamnolipids on the S2b systems is significantly lower than from that of the S7b system, but compared to the initial state (Figure 3) an increase of the  $\Delta\phi^*$  value is observed for this system as well. Hence, the initial wetting preference of the hydrates are shifted from water wet to intermediate wet upon the addition of rhamnolipids.

### The effect of naphthenic acids

The effect of the naphthenic acid fractions on crude oil/brine emulsion behaviour were tested in crude

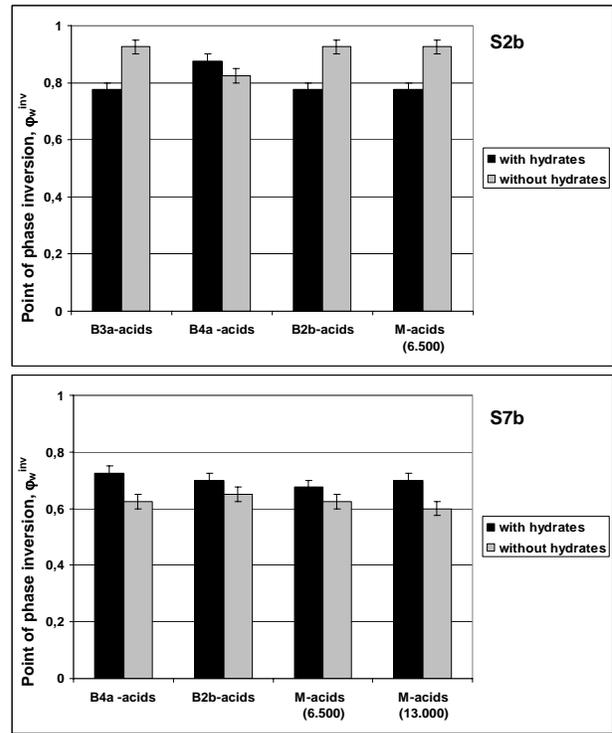


Figure 7: Upper:  $\phi_w^{inv}$  for S2b system containing naphthenic acid fractions. With hydrates (black), without hydrates (grey). Lower:  $\phi_w^{inv}$  for the S7b system containing naphthenic acid fractions.

oils S2b and S7b, with and without freon hydrates. All the acid fractions were added to the crude oils in the concentration of 6.500ppm. The M-acids were also tested at twice this concentration (13.000ppm) in the S7b oil. The results are given in Figure 7. The normalised differences in the inversion points with and without hydrates are given in Figure 8 (normalised according to Equation 1).

Similar to the water soluble additives, it is observed that the addition of acid fractions significantly alter the inversion behaviour of the emulsions compared to the original emulsions without additives (see Figure 3). This indicates an alteration of the wettability of the hydrate particles generated in the modified systems compared to their initial state. In general, for S7b the addition of acids increase  $\phi_w^{inv}$  for hydrate containing systems compared to systems without hydrates, giving positive  $\Delta\phi^*$  values and hence an indication of oil wet hydrates (Figure 8). For the S2b oil, however, the addition of acid fractions has an opposite effect. The  $\phi_w^{inv}$  for hydrate containing systems are generally lower than for the

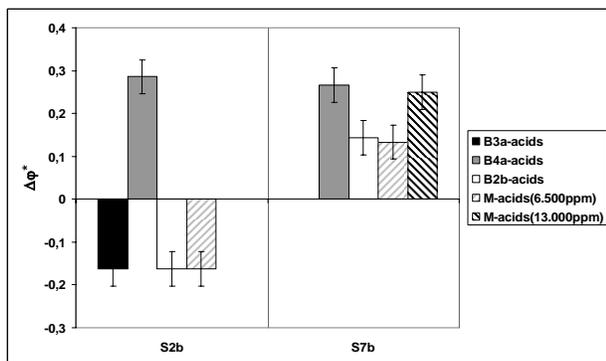


Figure 8: The effect of naphthenic acids on emulsion behaviour. Acids extracted from B3a (black), B4a (grey), from B2b (white), and from an acidic oil fraction received from Mongstad (6.500ppm: hatched in grey, and 13.000ppm: hatched in black). The differences in points of phase inversion with and without hydrate particles are normalised according to Equation 1.

systems without hydrates, giving negative  $\Delta\phi^*$  and hence an indication of water wet particles. Compared to the initial state of the S2b system (Figure 3), the acids seem unable to alter the wettability of the hydrates generated in this system. The B4a-acid fraction is an exception, giving a significant positive  $\Delta\phi^*$  value, indicating oil wet hydrates.

## Summary of observations

For the majority of the investigated systems, the chemical additives strongly affect the emulsion behaviour, compared to corresponding systems without additives. The effects are attributed to wetting alteration of the hydrate particles generated in the systems. The wetting alteration towards oil wet behaviour can be explained by adsorption of the additive to the hydrate surface: polar groups associated with the hydrate surface and lyophilic parts associated with the liquid phases.

It is noted that the modification of two crude oil/brine systems by one additive may cause distinctly different results. For 5 systems out of a total of 17 systems investigated, the alteration towards oil wet behaviour is not observed. In some cases, the additives show no impact on the initial wetting preference of the hydrates.

For efficient adsorption of additives to hydrates to occur, the hydrate particle must be easily contacted by the additive, a situation best obtained when the

chemical is added to the bulk phase in which the major part of the particle surface resides, and thereby also the majority of the available adsorption sites. Hence, the initially water wet S2b and S3b systems are rendered oil wet by the water soluble polymer HPMC, while the initially intermediate wet S7 systems are essentially unchanged (Figure 4). Further, 4 out of 5 naphthenic acid fractions added to the S2b oil phase (Figure 8), i.e. acting from the "oil side", were unable to alter the initial water wet property of the hydrates. The fifth fraction, the B4a-acids, did cause such a change, and probably contain specific molecular compounds with particular affinity for the hydrate surfaces, giving positive  $\Delta\phi^*$  in spite of non-favourable initial conditions for adsorption. For the S7b oil, generating initially intermediate wet hydrates, more adsorption sites are available in the bulk oil phase compared to the water wet hydrates of S2b, and all the naphthenic acid fractions are able to alter the wettability towards more oil wet behaviour. Finally, the additive must be available at sufficient concentrations. For both rhamnolipids (Figure 6) and M-acids (Figure 8) an increase in the additive concentration resulted in increasing  $\Delta\phi^*$  values. The negligible effect of surfactin (Figure 5) may be due to a too low concentration.

## Correlation to plugging tendency

A summary of the tests in the sapphire cell is given in Table 2. All additive-free systems form hydrate aggregates. For oil S2b, only the B4a acids were able to produce a disperse hydrate system. The other oil soluble additives did not significantly change the behaviour of the hydrates formed in this oil, nor did the water soluble additives. For oil S7b, only the rhamnolipid was able to produce a disperse hydrate system.

A comparison may now be made between the plugging tendency tests and the emulsion inversion point tests for several oil/water/additive systems. The results of the emulsion tests are included in Table 2, together with an answer as to whether a correlation is found. There is a positive correlation for 9 out of 11 systems, in the sense that water wet and intermediate wet hydrates from the emulsion method corresponds to plugging systems, whereas oil wet hydrates from the emulsion method correspond to dispersed systems. Both deviations are observed for water soluble additives in formation water.

Table 2: Correlations between plugging tendency tests and emulsion tests. Brine is 3.5 % NaCl solution, and sfw is a synthetic formation water matching the S2b production stream.

Oil	Water	Additive	Plugging tendency	$\Delta\phi^*$	Corr [Y/N]
S2b	sfw	-	Plug	-	-
S2b	ssw	-	Plug	-0.12	Y
S2b	sfw	HPMC	Plug	0.36	N
S2b	ssw	rh.lip.	Plug	-0.06	Y
S2b	ssw	B3a acids	Plug	-0.16	Y
S2b	ssw	B4a acids	Dispersion	0.26	Y
S2b	ssw	B2b acids	Plug	-0.16	Y
S2b	ssw	M-acids	Plug	-0.16	Y
S7b	sfw	-	Plug	-	-
S7b	ssw	-	Plug	0.00	Y
S7b	ssw	HPMC	Plug	-0.05	Y
S7b	ssw	rh.lip.	Dispersion	0.52	Y
S7b	sfw	rh.lip. + cosurf	Plug	0.35	N

From the emulsion method, the addition of 500ppm rhamnolipids was found to impose different effects in S7b and in S2b. This was surprising in the sense that the two oils are similar with respect to characteristic crude oil properties, although they generate hydrates of slightly different wettabilities (intermediate wet and weakly water wet). Interestingly, the plugging experiments revealed the same differentiation, as S7b became dispersed whereas S2b remained plugging or, in fact, became more aggressively plugging on addition of rhamnolipids. The reasons for this unexpected behaviour is probably connected to small differences in the interfacial tensions in the two systems. This will be discussed in some detail below.

The addition of B4a-acids to S2b resulted in a significant positive  $\Delta\phi^*$  value. This system is identified as disperse in the sapphire cell tests, hence a positive correspondence is observed. Also, the addition of B3a-acids, B2b-acids and M-acids, with significant negative  $\Delta\phi^*$  values, turned out with positive correspondence, i.e. as plugging systems.

The system containing rhamnolipid and berol, and one system containing HPMC did not show correspondence between emulsion behaviour and plugging tendency. For both systems, a significant positive  $\Delta\phi^*$  was observed, yet the systems were identified as plugging. A possible explanation for this will be outlined below.

## Wetting diagrams

An important difference between the emulsion tests and the plugging tendency tests is that the hydrate forming component is Freon in the former case, but a natural gas mixture in the latter case. Hence, a direct comparison of the two methods should be made with care. In both cases, structure II hydrates are formed, and there is no reason to assume that the physical properties of the hydrates formed in the two methods are differing. The hydrate formers will on the other hand have an impact on the interfacial tensions<sup>1</sup> in the system.

Assuming that hydrate formation is an interfacial process [18], there are three interfacial tensions involved: oil/water, hydrate/water and hydrate/oil. Assuming further that the hydrate nucleus is lens-shaped and using Neumanns triangle, the correlation between the three interfacial tensions can be illustrated in wetting diagrams, an example of which is shown in Figure 9. The interpretation and use of wetting diagrams is discussed further in Fotland and Askvik [19].

Figure 9 illustrates the range of valid hydrate/oil and hydrate/water interfacial tensions for which a hydrate nucleus may exist at an oil/brine interface, the oil/water interfacial tension in Figure 9 is 20 mN/m.

<sup>1</sup>The term interfacial tension is properly used only in liquid/liquid systems. In a solid/liquid system, surface energy is the preferred term. We will for simplicity use the interfacial tension, regardless of the aggregate state of the bulk phases involved

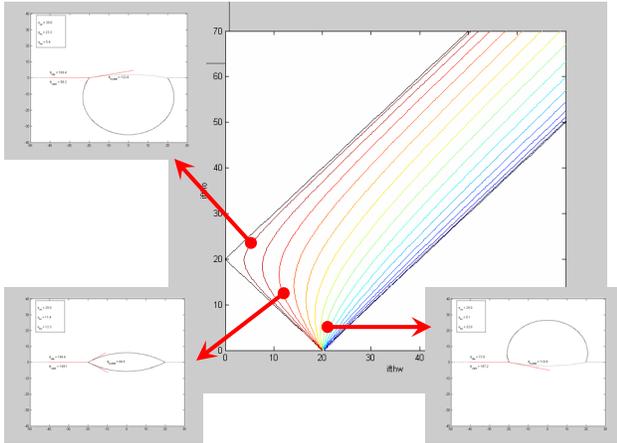


Figure 9: Theoretical wetting diagram, hydrate/oil interfacial tension ( $\sigma_{ho}$ ) as a function of hydrate/brine interfacial tension ( $\sigma_{hw}$ ), for a hydrate nucleus at an oil/brine interface. Oil/brine interfacial tension,  $\sigma_{ow} = 20$  mN/m. The shape of the nucleus at three different positions in the diagram is indicated. Upper left: Water wet, Low left: Intermediate wet, and Low Right: Oil wet hydrate. The isolines within the diagram describes the alteration of hydrate-oil wetting angles (measured through the oil phase) as a function of  $\sigma_{hw}$  and  $\sigma_{ho}$ .

The area is bounded by three lines, the lines defining spreading conditions in the system. Antonow's rule applies at these lines, i.e. one interfacial tension is expressed as the sum of the two others. At the lower right border, the hydrate/water interfacial tension is the sum of the oil/water and the hydrate/oil interfacial tensions. Physically, this corresponds to a situation where oil is the spreading phase, and there is no (or minimum) contact between hydrate and water. Similarly, water is the spreading phase at the upper left border, and hydrate is the spreading phase in the lower left border.

The isolines in Figure 9 describes the wetting angle of the lens through the oil phase. Although we note the singularity at zero hydrate/oil interfacial tension, the trend is that the oil wetting angle increases from  $0^\circ$  at the oil spreading border (lower right) to  $180^\circ$  both at the water spreading border (upper left) and at the hydrate spreading border (lower left). Inset in Figure 9 are illustrations of the shapes of the hydrate nuclei at three different sets of hydrate/oil and hydrate/water interfacial tensions.

Assuming now that the microscopic interfacial tensions of the hydrate nucleus corresponds well with the macroscopic values, it becomes possible that

small changes in interfacial tensions can cause large changes in wetting behaviour, and hence the outcome of experimental tests as presented in this paper. This will in particular be true if the system has interfacial tensions defining a state in the vicinity of either border of the wetting diagram.

In Figure 9, the oil/water interfacial tension is constant at 20 mN/m. In Figure 10, the wetting diagram of a 5 mN/m oil/water interfacial tension system is shown in addition to the system from Figure 9. The oil wetting angle isolines are shown for both systems. We note that the system having low oil/water interfacial tension has a small valid area of hydrate/water and hydrate/oil interfacial tensions. A direct implication of this is that the oil wetting angle isolines are very close to each other, and hence that the wetting state of this system is more sensitive to small changes in interfacial tensions than in the initial system. The significance of this issue becomes more prominent as the oil/water interfacial tension decreases. This means that for systems of very low oil/water interfacial tensions, freon and natural gas systems may be very hard to compare due to the different effect the two hydrate formers have on the interfacial tensions of the systems. We note however that systems of higher interfacial tensions have large valid areas in the wetting diagram. Such systems will therefore be more robust, and be more likely to give corresponding results.

The crude oil/brine interfacial tensions must thus be regarded as an important parameter when it comes to comparing the emulsion method to plugging experiments. The presence of freon has been found to slightly increase the interfacial tension between toluene and brine, giving an increase of 1 mN/m for a 50:50 mixture (by volume) of toluene:freon compared to pure toluene. Typical values of crude oil/ brine interfacial tensions are in the approximate range from 15 mN/m to 40 mN/m. Within these values, small alterations are not critical, and the observations from the emulsion method and from the plugging experiments have been found to coincide [4]. When chemical additives are introduced, however, the oil/brine interfacial tension may be significantly altered. For example, the interfacial tension between S7b and 500ppm aqueous solution of rhamnolipid is approximately 1 mN/m in 3.5wt% NaCl(aq), and approximately 0.6 mN/m in formation water (containing Berol 160). The correspon-

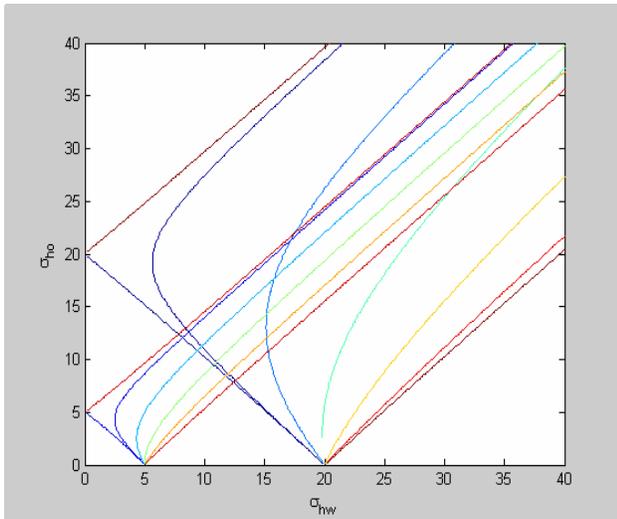


Figure 10: Theoretical wetting diagram, hydrate/oil interfacial tension ( $\sigma_{ho}$ ) as a function of hydrate/brine interfacial tension ( $\sigma_{hw}$ ), for a hydrate nucleus at an oil/brine interface. Oil/brine interfacial tensions,  $\sigma_{ow} = 20$  mN/m and 5 mN/m. Isolines for the hydrate-oil wetting angle (measured through the oil phase) is given.

dence at these low values thus appears random, and is observed to be positive in the former case and negative in the latter.

The emulsion tests show that HPMC has a capacity for producing oil wet hydrates, at least for one of two oils. Neither oil was rendered dispersive by HPMC in the plugging tendency tests, however. HPMC does not lower the oil/water interfacial tension, so this discrepancy must have an explanation other than in the discussion given above. HPMC is a water soluble polymer of moderately high molecular weight. It is therefore possible that polymer-specific mechanisms play a role, such as depletion flocculation, bridging flocculation and steric stabilization, and that the balance of these mechanisms changes with the shift in experimental conditions. The data set is not large enough however to shed light on this matter.

The addition of petroleum acids to crude oils in the concentrations investigated here does not lower the oil/brine interfacial tension to the extent of the water soluble additives, and the systems modified by petroleum acids show positive correspondence.

## CONCLUSIONS

Hydrate wettability is found to be a governing parameter for hydrate morphology and hence, the hydrate plugging tendency. It has been observed that the wettability of petroleum hydrates is significantly altered on addition of chemical additives at low concentrations. In two cases, a shift in hydrate plugging tendency from plugging to dispersed hydrate systems at realistic conditions have been observed, one for a petroleum acid fraction and one for a bio-surfactant structure.

The chemical effect is crucially dependent on crude oil composition, and thus the initial state of the hydrates, as the same additive may give different effects in two different crude oil systems when compared at otherwise equal conditions. This observation applies both for hydrate wettabilities determined from emulsion behaviour, and for natural gas hydrate plugging tendencies at realistic conditions. It is further observed that the link between laboratory tests using freon hydrates and natural gas hydrates at realistic conditions is crucially dependent on the interfacial tensions in the two systems. At low crude oil/brine interfacial tension, small changes in solid/fluid interfacial tensions is critical for the wettability of the hydrate particles, and thus the plugging tendency of the system.

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