An evaluation of emerging technologies in kinetic inhibitors incorporating various amphiphilic molecules to reveal interactions and possible synergies in those, intended for use in an aqueous base drilling fluid.

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ABSTRACT

Gas hydrates are ice-like solids that form from natural gas and water under high pressures and low temperatures. The potential formation of gas hydrates is an increasing problem as water-based fluid systems are more frequently used for deepwater drilling in the North Sea Region. Water-based drilling fluids are preferred rather than oil-based ones due to their low toxicity to the environment. The large water content of these drilling fluids is an excellent source for gas hydrates to be formed. Today, thermodynamic inhibitors such as monoethylene glycol (MEG) and KCl are the only sufficient inhibitors used. A high salt content will make the density too high to be used in low-density drilling fluids for deepwater drilling. The use of MEG presents unwanted reactions with kaolinite- and illite-rich clays and has dispersive effects on these formations, causing frequent problems with bit balling and high dilution rates. MEG is also used in large dosages and is toxic to the environment. The use of low dosage kinetic inhibitors is commonly employed in drilling fluids today due to their lower dosages and low toxicity. The problem with using these types of inhibitors is that they do not provide a sufficient amount of subcooling under these extreme conditions. The background for this project was to investigate a broader range of gas hydrate inhibitors to replace the traditionally used thermodynamic inhibitors, in search for fluids which could handle these new challenges.

In this project gas hydrate formation temperatures were obtained by using Physica rheometer modified for gas hydrate testing. The tests were performed in a low-inhibited water-based drilling fluid; Glydril 1,1SG. Hydrate formation temperatures were obtained from the base fluid (an average of 7,2°C) and from the base fluid with 6000ppm and 12000ppm of the kinetic hydrate inhibitor Luvicap 55w (average additional subcoolings of 4,7°C and 5,4°C respectively). These results were used for comparison when adding different surfactants prior to the KHI to the base fluid. A 12000ppm concentration in total was set as a maximum value as this is a suitable dosage for use in a drilling fluid, calculated based on the water content. The surfactants tested for synergy effects with Luvicap 55w in this project were: the cationic surfactant Arquad 12-30, the anionic surfactant SDS, the amine oxide Aromox C-12/W and the non-ionic surfactant Imbentin-AG/124S/040. Two anti-agglomerants designed by M-I SWACO (Cdld-151 and Cdld-445) were also tested due to their surfactant nature. The surfactants were tested at 6000ppm and 12000ppm alone, and at a 6000ppm/6000ppm ratio with Luvicap 55w to look for possible synergy effects. Two parallels were measured for each combination. The AA´s were only added in combination with Luvicap 55w at the same ratio.

Hydrate growth in the base fluid with Luvicap 55w was clear and sudden and at a specific temperature. Hydrate growth in samples with only the surfactants appeared to be gradual and random. This may be due to the dynamic process of micellization. This phenomenon seemed to be independent of surface charge and concentration. A higher concentration of surfactant generally increased the hydrate formation temperature which indicates that the CMC is an important factor in creating nucleation sites. The only surfactant that appeared to provide additional subcooling to the base fluid on its own was Arquad 12-30 (when added at 6000ppm, 1,2°C). The other surfactants raised the hydrate formation temperatures of the base fluid when added alone.

When the surfactants were added together with Luvicap 55w, the KHI generally seemed to stabilize the surfactant, and hence the hydrate growth became more sudden and at a specific temperature. This may be due to the preferred binding of KHI to the water phase or the binding of surfactant to the KHI. The AA´s did not seem to be stabilized in the same matter and the hydrate growth was gradual and unstable together with Luvicap 55w. The 6000ppm/6000ppm ratio of Luvicap 55w in combination with Arquad 12-30, SDS, Aromox C-12/W and Imbentin-AG/124S/040 presented average additional subcoolings of 10,6^{o}C, 4,4^{o}C, 4,0^{o}C and 2,7^{o}C respectively. Both AA´s presented additional subcoolings of 1,5^{o}C. In comparison to the 6000ppm addition of only Luvicap 55w, this indicates antagony effects or no effects at all for all additives except from Arquad 12-30. Tests were also performed by adding the KHI prior to Arquad 12-30 in the 6000ppm/6000ppm ratio, to see if the order of addition affected the additional subcooling provided by this combination. This presented an average additional subcooling of 6,9^{o}C. As the 6000ppm/6000ppm ratio of Arquad 12-30 added prior to the KHI presented excellent results, other concentration ratios were tested to see if this could provide even more subcooling due to a higher degree of synergism. The other ratios of Luvicap 55w and Arquad 12-30 tested were 9000ppm/3000ppm, 3000ppm/9000ppm, 7000ppm/5000ppm and 5000ppm/7000ppm, which presented average additional subcoolings of 5,5^{o}C, 7,4^{o}C, 6,2^{o}C and 7,1^{o}C respectively. The 1:1 ratio thus seemed to provide the best degree of additional subcooling.

The main conclusions drawn from these results are that a cationic surfactant with a smaller head group such as Arquad 12-30 seems to provide most additional subcooling. The headgroup of Arquad 12-30´s contains tri-methyl groups while the headgroup of the AA´s contains tri-butyl groups. The AA´s presented much poorer results in providing additional subcooling despite its cationic nature. The synergy effects and the additional subcooling provided from the 6000ppm/6000ppm Luvicap 55w/Arquad 12-30 combination, appear to provide the double that of 12000ppm of Luvicap 55w. The reason for this may be due to coating of negative particles in the drilling fluid (such as barite, xanthan gum and carboxymethyl cellulose), and hence an enhanced effect of the KHI in the water phase. In theory the KHI will bind to both particles and the water phase. The antagony effects present by the addition of the other surfactants/anti-agglomerants in combination with Luvicap 55w may be due their lack of binding to particles due to their surface properties, and hence enhanced micellization and creation of nucleation sites.

The 12000ppm Luvicap 55w and 6000ppm/6000ppm ratios of Luvicap 55w and the different surfactants/anti-agglomerants were also tested for compatibility with the base fluid. Standard WBM tests showed that the additives did not induce any major differences in properties that cannot easily be adjusted back to the original parameters/properties.

The ratio of 6000ppm/6000ppm of Luvicap 55w and Arquad 12-30, where the surfactant is added prior to the KHI, appears to be the best combination. The results from the other ratios tested indicate that a higher concentration of the surfactant (hence particle coating) is a more critical factor than a higher concentration of KHI. Arquad 12-30 is commercially available, but further tests need to be performed. It is suggested to test more parallels and check the results´ validity by statistical tests, perform adsorption studies to confirm the theories presented in this study, test in other fluid systems, test with other ratios near the 6000ppm/6000ppm ratio, test 1:1 ratios at lower concentrations and test if the effect last/is

stable over time. Arquad 12-30 is classified as a red product according to the HOCNF and hence the substance cannot be used as an oil field chemical in WBM. Alternatives to Arquad 12-30 need to be identified, which may be accomplished with in-house (M-I PT) synthesis of analogues. The excellent result of 6000ppm/6000ppm of Luvicap 55w and Arquad 12-30 could potentially reduce the use of THI significantly in DW WBM for use in deepwater drilling.

SAMMENDRAG

Gasshydrater er et is-liknende faste stoffer som dannes som følge av at naturgass og vann reagerer under høyt trykk og lav temperatur. Faren for potensiell dannelse av gass hydrater er et økende problem ettersom vannbaserte væskesystemer blir mer og mer hyppig brukt ved dypvannsboring i Nordsjøen. Vannbaserte borevæsker er mer foretrukket enn oljebaserte borevæsker på grunn deres lave giftighet for miljøet. Det høye vanninnholdet i disse borevæskene er en utmerket kilde til dannelse av gasshydrater. I dag brukes termodynamiske inhibitorer som monoetylen glykol (MEG) og KCl. Disse er de eneste tilstrekkelige inhibitorene. Et høyt saltinnhold vil gi en for høy tetthet til å bli brukt i lav-tetthets borevæsker for dypvannsboring. Bruken av MEG vil gi uønskede reaksjoner med kaolinitt- of illitt-rike leirer og har dispergerende effekt på disse formasjonene, noe som vanligvis forårsaker problemer med agglomerering av borekaks på borekronen og høye fortynningsrater. MEG blir også brukt i høye doser og er giftig for miljøet. Bruken av lav-dose kinetiske inhibitorer er vanligvis brukt i borevæsker idag på grunn av deres lave dosering og lave giftighet. Problemet ved bruken av disse inhibitorene er at de ikke gir en høy nok grad av ”subcooling” under disse ekstreme forholdene. Bakgrunnen for dette prosjektet var å undersøke et bredere utvalg av gasshydrat-inhibitorer for å erstatte de tradisjonelt brukte termodynamiske inhibitorene, for å finne væsker som kan takle disse nye utfordringene.

I dette prosjektet ble gasshydrat dannelsestemperaturer funnet ved å bruke Physica rheometer modifisert for gasshydrat testing. Testene ble utført i en lav-inhibert vannbasert borevæske; Glydril 1,1SG. Dannelsestemperaturene ble funnet for basevæsken (et gjennomsnitt på 7,2^{o}C) og for basevæsken med 6000ppm og 12000ppm av den kinetiske gasshydrat inhibitoren Luvicap 55w (en gjennomsnittlig ekstra ”subcooling” på henholdsvis 4,7^{o}C og 5,4^{o}C). Disse resultatene ble brukt for å sammenlikne med tilsetning av forskjellige surfaktanter tilsatt før KHI i basevæsken. En konsentrasjon på 12000ppm ble satt som en maksimal verdi da dette er en passende konsentrasjon til bruk i en borevæske. Konsentrasjonen er kalkulert på bakgrunn av vanninnholdet i borevæsken. Surfaktantene som ble testet for synergieffekter med Luvicap 55w i dette prosjektet var: den kationiske surfaktanten Arquad 12-30, den anioniske surfaktanten SDS, amin oksidet Aromox C-12/W of den ikke-ioniske surfaktanten Imbentin-AG/124S/040. To anti-agglomeranter designet av M-I SWACO (Cdld-151 og Cdld-445) ble også testet på bakgrunn av deres surfaktant egenskaper. Surfaktantene ble testet ved konsentrasjonene 6000ppm og 12000ppm alene, og ved et 6000ppm/6000ppm forhold med Luvicap 55w for å se på eventuelle synergieffekter. To paralleller ble målt for hver kombinasjon. Anti-agglomerantene ble kun målt i kombinasjon med Luvicap 55w ved samme fohold.

Hydratveksten i basevæsken med Luvicap 55w var klar, plutselig og ved en spesifikk temperatur. Hydratveksten i prøvene med bare surfaktant viste seg å være gradvis og tilfeldig. Dette kan være på grunn av micellisering som er en dynamisk prosess. Dette fenomenet virket som det var uavhengig av overflateladning og konsentrasjon hos surfaktanten. En høyere konsentrasjon av surfaktant økte generelt sett hydrat dannelsestemperaturen, noe som indikerer at CMC er en viktig faktor i dannelse av nukleasjonsseter. Den eneste surfaktanten som viste seg å gi noe ekstra ”subcooling” alene

til basevæsken, var Arquad 12-30 (ved 6000ppm, 1,2°C). De andre surfaktantene økte hydrat dannelsestemperaturen i basevæsken når de ble tilsatt alene.

Når surfaktantene ble tilsatt sammen med Luvicap 55w, viste den kinetiske inhibitoren seg generelt sett til å stabilisere surfaktanten. Det vil si at hydrat veksten ble mer plutselig og ved en spesifikk temperatur. Dette kan være på grunn av foretrukket binding av KHI til vannfasen eller binding av surfaktant til KHI. Anti-agglomerantene virket ikke som de ble stabilisert på samme måte, og hydratveksten var gradvis og ustabil sammen med Luvicap 55w. Forholdet 6000ppm/6000ppm av Luvicap 55w i kombinasjon med Arquad 12-30, SDS, Aromox C-12/W og Imbentin-AG/124S/040 gav gjennomsnittlig ekstra ”subcooling” på henholdsvis 10,6°C, 4,4°C, 4,0°C og 2,7°C. Anti-agglomerantene gav begge ekstra ”subcooling” på 1,5°C. I sammenlikning med tilsetning av konsentrasjonen på 6000ppm av kun Luvicap 55w, så indikerer dette antagonieffekter eller ingen effekt i det hele tatt for alle surfaktanter/anti-agglomeranter untatt Arquad 12-30. Tester ble også utført ved å tilsette den kinetiske inhibitoren før Arquad 12-30 i et konsentrasjonsforhold på 6000ppm/6000ppm, for å se om rekkefølgen av tilsetningen ville påvirke den ekstra ”subcoolingen” gitt av denne kombinasjonen. Dette gav en gjennomsnittlig ekstra ”subcooling” på 6,9°C. Konsentrasjonsforholdet 6000ppm/6000ppm gav svært gode resultater, og dermed ble andre konsentrasjonsforhold testet for å se om dette kunne gi en høyere grad av ”subcooling” som følge av en høyere grad av synergisme. De andre konsentrasjonsforholdene av Luvicap 55w og Arquad 12-30 som ble testet var 9000ppm/3000ppm, 3000ppm/9000ppm, 7000ppm/5000ppm og 5000ppm/7000ppm. Disse gav gjennomsnittlig ekstra ”subcooling” på henholdsvis 5,5°C, 7,4°C, 6,2°C og 7,1°C. Det viste seg altså at et 1:1 forhold gav den beste graden av ekstra ”subcooling”

Hovedkonklusjonene fra resultatene er at en kationisk surfaktant med en mindre hodegruppe, som Arquad 12-30 synes og gi mest ekstra ”subcooling”. Hodegruppen til Arquad 12-30 inneholder tri-metyl grupper, mens hodegruppene til anti-agglomerantene inneholder tri-butyl grupper. Anti-agglomerantene gav mye dårligere resultater med hensyn til ekstra subcooling til tross for sin kationiske karakter. Synergieffektene og den ekstra ”subcoolingen” fra konsentrasjonsratioen 6000ppm/6000ppm av Luvicap 55w/Arquad 12-30 kombinasjonen, virker å gi det dobbelte av hva 12000ppm av Luvicap 55w gav. Grunnen til dette kan være at surfaktanten dekker de negative partiklene i borevæsken (som baritt, xantangummi og karboksymetyl cellulose), og at KHI som følge av dette vil øke sin effekt i vannfasen. Teoretisk sett vil KHI bindes til både partiklene og vannfasen. Antagonieffektene som viser seg ved tilsetning av de andre sufaktantene/anti-agglomerantene i kombinasjon med Luvicap 55w skjer trolig ved at disse bindes dårlig til partiklene på grunn av overflateegenskapene, og derfor økt micellisering og dannelse av nukleasjonsseter.

Konsentrasjonsforholdene 12000ppm Luvicap 55w og 6000ppm/6000ppm av Luvicap 55w og de forskjellige surfaktantene/anti-agglomerantene ble også testet for kompatibilitet med base væsken. Standard WBM tester viste at disse stoffene ikke forårsaket noen store endringer i egenskaper. Endringene kan enkelt kan bli justert tilbake til de originale parametrene/egenskapene.

Konsentrasjonsforholdet 6000ppm/6000ppm av Luvicap 55w og Arquad 12-30, hvor surfaktanten ble tilsatt før KHI, synes å være den beste kombinasjonen. Resultatene fra de andre forholdene som ble testet indikerer at en høyere konsentrasjon av surfaktant (dekking

av partikler) er en mer kritisk faktor enn en høyere konsentrasjon av KHI. Arquad 12-30 er kommersielt tilgjengelig, men ytterligere tester må utføres. Det anbefales å teste flere paralleller og sjekke resultatenes gyldighet ved statistiske tester, utføre adsorpsjonsstudier for å bekrefte antagelsene i denne studien, teste i andre væskesystemer, teste andre konsentrasjonsforhold nær 6000ppm/6000ppm, teste 1:1 forholdet ved lavere konsentrasjoner og teste om effekten holder seg/er stabil over tid. Arquad 12-30 er klassifisert som et rødt produkt i henhold til HOCNF og dermed kan stoffet ikke bli brukt i WBM. Det må letes etter alternativer til Arquad 12-30, hvor syntetisering av analoger er en mulighet (M-I PT). De svært gode resultatene som ble funnet ved tilsetning av konsentrasjonsforholdet 6000ppm/6000ppm av Luvicap 55w og Arquad 12-30 kan potensielt redusere bruken av THI betydelig i DW WBM for bruk i dypvannsboring.

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Nomenclature

AA – Anti Agglomerant
AHR – After Hot Rolling
API – American Petroleum Institute gravity
BHR – Before Hot Rolling
BOP – Blow Out Preventer
CMC – Critical Micelle Concentration
DW – Deepwater
HOCNF – Harmonized Offshore Chemical Notification Format
KHI – Kinetic Hydrate Inhibitor
LDHI – Low-Dosage Hydrate Inhibitor
MEG – Monoethylene Glycol
OBM – Oil-Based Mud
PVCap – Poly-N-Vinyl-N-Caprolactam
PVP – Poly-N-Vinyl-Pyrrolidone
PT – Product Technologies
R&D – Research and Development
ROP – Rate of Penetration
THI – Thermodynamic Hydrate Inhibitor
WBM – Water-based Mud

1 INTRODUCTION

Water-based drilling fluids are primarily chosen for drilling of deep water wells in the North Sea region, and thermodynamic inhibitors like monoethylene glycol (MEG) and KCl are the only sufficient hydrate inhibitors used. With the exploration in deeper waters there is an increased demand for hydrate inhibitive drilling fluids with lower density than those typically formulated with high salt concentrations. Use of MEG is occasionally also a controversial choice while drilling kaolinite- and illite-rich clays, as the glycol has dispersive effect on those formations causing frequent problems with bit balling and high dilution rates. The environmental impacts, the high dosages used, and the high costs associated with MEG present additional disadvantages. The background for this project was to investigate a broader range of gas hydrate inhibitors to replace traditionally used thermodynamic inhibitors in search for fluids which can handle those new challenges.

2 LITERATURE REVIEW

2.1 Drilling fluids

Drilling fluids (Figure 1) are essential in drilling operations due to their many important functions. With the help of good quality drilling fluids oil and gas will be produced efficiently and safe. The main function of the drilling fluids is to control well conditions. The well conditions determine the necessary properties of the drilling fluid, different wells may have completely different requirements. In addition, different types of drilling fluids can be used for different sections of the same well during a drilling operation. Some properties will be more important than others depending on the well conditions (SWACO 1998).

Figure 1: Freshly mixed drilling fluid (Glydril).

2.1.1 Functions of drilling fluids

Removal of cuttings

During a drilling operation cuttings from the formation needs to be removed from under the drill bit and out of the well. Drilling fluid is distributed down the drill string, through the drill bit and will carry the cuttings up through the annulus (Figure 2) and up to the surface. The most important drilling fluid properties due to cuttings removal are viscosity, density and annular velocity. In general, a high-viscosity fluid will have the best performance because cuttings will settle slowly and will easily be circulated out of the well (SWACO 1998). On the other hand, cuttings need to be removed immediately from under the drill bit and into the annulus, which requires a low-viscosity drilling fluid. This will increase the efficiency and speed of the drilling process, and also prevent the cuttings from being crushed into smaller pieces which will make removal more difficult. The cuttings will sink according to gravity and ascend according to the circulative movement of the drilling fluid. The annular velocity is the difference between these two forces. The viscosity and density of the drilling fluid decides how the cuttings are lifted and their buoyancy respectively. It's important that the drilling fluid has sheer thinning properties, which means that it has low viscosity at the drill bit and high viscosity at the annulus. High concentrations of cuttings and solids will increase the drilling fluids weight and viscosity. This will affect rotation, circulation, filter-cake thickness, torque and drag significantly (Skjeggestad 1989).

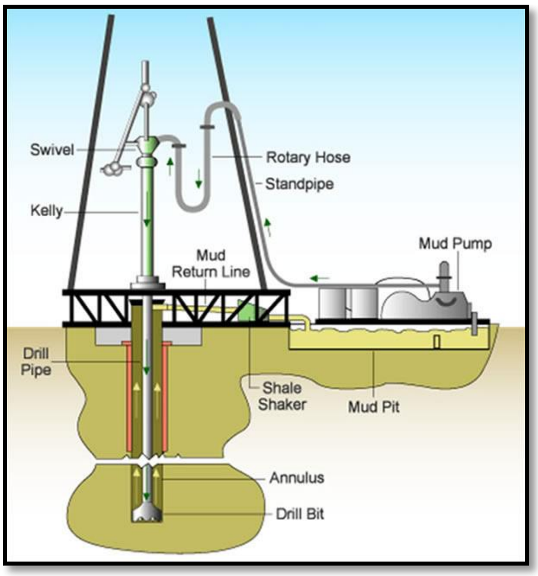


Figure 2: Drilling fluid circulation in a drilling operation (Online 2011).

Formation pressure control

The formation consists of pores filled with gas and liquid that is under pressure from the formation. If this pressure is not controlled it can result in leakage into the borehole (Skjeggestad 1989), lost circulation, borehole instability, stuck pipe (SWACO 2011b) or a dangerous situation like a blowout (SWACO 1998). The hydrostatic pressure from the drilling fluid needs to be higher than the formation pressure. The hydrostatic pressure is proportional with the depth of the borehole and the density of the drilling fluid. In addition, circulation and also when the drill string is pushed in and drawn out of the hole it will create pressure differences. All these pressure differences need to be balanced by the drilling fluids density (Skjeggestad 1989).

Thixotropic properties

The drilling fluid have to have thixotropic properties, which means that it will make a gel structure when the drilling stops and the fluid is static. The circulation stops many times during a drilling operation and cuttings and weight material needs to stay suspended during this period. The gel has to be reversible when the circulation starts up again (Skjeggestad 1989).

Fluid loss and filter-cake

A permeable formation together with a high hydrostatic pressure will force the drilling fluid to penetrate the formation. Most of the drilling fluid will be kept in the system due to the filtrating properties of the formation, but some fluid will be lost and a filter-cake will be formed on the walls of the borehole. These filter-cakes have to have low permeability and thus prevent additional fluid loss. Fluid loss to the formation can affect logging, testing and drilling fluid properties (Skjeggestad 1989). Filtrate may also destabilize and damage the formation (SWACO 2011b). A thin filter-cake is preferred because a thick filter-cake will reduce the size of the borehole and hence make drilling more difficult (Skjeggestad 1989). Fluid loss additives and bridging material can be added to improve cake quality. If bridging fails, whole mud can penetrate the formation and the pressure may be high enough to fracture the rock. In this case circulation will be lost, and generally a damaged formation will create unstable conditions like formation caving (SWACO 2011b).

Protect the formation

The formation stabilizes the borehole and needs to be protected (Skjeggestad 1989). Mechanical stress or chemicals may interfere with the porosity and permeability of the formation and thus change its properties (SWACO 1998). The chemicals in the drilling fluid should not react with the formation in a way that will make it unstable. Water present in the drilling fluid for instance, will make clay and shale swell and thus cause tension and structure change in the formation. In addition, interactions with the formation will cause poor cuttings- and core samples for testing and information (Skjeggestad 1989). Lubricants and other additives may mask indications of hydrocarbons present (SWACO 1998). Interactions can be controlled with the addition of chemical inhibitors and additives (Skjeggestad 1989).

The weight of the drilling fluid must be able to balance the mechanical forces on the wellbore. If the formation is damaged and the borehole is enlarged it will have disadvantages such as low annular velocity and high cementing costs. A good quality filter-cake may limit enlargement (SWACO 1998).

Buoyancy to drill string and casings

The drill string and the casings are extremely heavy. If the drilling fluid is able to create enough buoyancy, it will prevent stretches in the surface equipment. The density of the drilling fluid creates buoyancy and lifts the equipment to relieve strain (Skjeggestad 1989). The buoyancy is equal to the weight of drilling fluid displaced by the equipment (SWACO 1998).

Cooling and lubrication

The drilling process will generate much heat due to friction. The formation is a poor heat absorber and thus the heat needs to be absorbed by the drilling fluid and transported out of the system. The drilling fluid must therefore have sufficient heat capacity and conductivity to cool down the equipment and transport the heat to the surface. The drilling fluid properties must withstand temperature increase. In addition, the drilling fluid must be able to lubricate the equipment, which again reduces heat due to friction (Skjeggestad 1989).

Corrosion control

Alkaline drilling fluids with $pH > 9, 5$ can be used to prevent corrosion on the equipment. In addition, an alkaline environment will reduce decomposition of organic substances which can produce corrosive gases (Skjeggestad 1989) like O_2, CO_2 and H_2S (SWACO 1998). Corrosion additives can be added to the drilling fluid (Skjeggestad 1989). Trapped oxygen conditions like foam are also corrosive. Foam can be removed by adding chemical inhibitors and scavengers (SWACO 1998). Corrosion will cause problems such as equipment failure and leaks (SWACO 2011b). In addition, the drilling fluid must not affect rubber (SWACO 1998) elastomers, or be erosive (SWACO 2011b).

Energy transmission

The drilling fluid must be able to transmit hydraulic energy to the equipment (SWACO 1998).

Environment

Local environmental restrictions have to be taken into account due to the wide range of different chemicals present in the drilling fluid. Minimum impact on the environment and minimum health hazards on employees is important. If the drilling fluid can be disposed of near the well site this will be the most advantageous, especially due to economics (SWACO 1998). Chemicals used in drilling fluids can be toxic, irritant and flammable and are associated with dusts and vapors (SWACO 2011b).

There are many properties that need to be maintained and it’s impossible to optimize every single property in the same drilling fluid. Compromises need to be made, and the focus is mainly on safety, economics and efficiency (Strand 1998).

There are primarily two types of drilling fluids or “muds” that are frequently used in drilling operations; oil-based muds and water-based muds.

The type of fluid used depends on the nature of the formation and the drilling conditions present. Waste disposal needs are also an important factor (Caenn et al. 2011).

2.1.2 Oil-based mud

Formations commonly consist of layers of reactive clay that will swell if there is water present in the system. It’s therefore desirable to use inhibitive muds. Oil-based muds (OBM´s) are inhibitive and will give maximum stability in clay formations, which is of particular importance in deviated wells. OBM´s will inhibit clay swelling due to the invert oil emulsion present. A semi-permeable layer of oil will cover the water droplets and while water can permeate this layer, salt cannot. The salinity level in the mud has to be the same as the salinity level in the formation, or else osmosis will remove water from the mud (Strand 1998). Emulsifying agents may help keep water in solution. In addition, OBM´s have excellent performance with regards to rate of penetration (ROP), wellbore stability, lubricity, thermal stability and has high tolerance for contaminations such as salts (Caenn et al. 2011), cement, H_2S etc. due to its non-polar nature. High drilling speed, less corrosion problems and no cuttings swelling are other advantageous properties of OMB´s (Strand 1998).

In OBM´s an oil phase is present. This oil phase may be diesel oil, mineral oils or low-toxicity mineral oils (Caenn et al. 2011). Diesel oil contains aromatics which can cause cancer and harm the environment, thus low-toxicity oils where most aromatics are removed are preferred. These oils have lower flash points and are not as easily vaporized as the diesel oil and mineral oils, which means less fire hazard and less impact on employees and environment (Strand 1998). In spite of this, the main disadvantage of using OBM´s is still the environmental hazards. Vapors, spilling and toxic cuttings that need extensive handling and disposal are just some of the OBM´s weaknesses (Strand 1998). In addition, environmental regulations are getting stricter (Caenn et al. 2011), as for example maximum oil content in cuttings which may limit use of OBM´s in the future (Strand 1998).

Table 1 presents the main components of OBM´s and functions of the different components.

Table 1: OBM´s – Main components and functions (SWACO 2011b). The table is edited.

OBM - Basics	
Oil Phase	Diesel, Mineral oil, Paraffin, Ester, Olefins
Brine Phase	$CaCl_2$, NaCl
Emulsifiers/Wetting agents	Fatty acids (Amidoamines, Imidazolines)
Density	Barite, $CaCO_3$, Hematite, Illmenite
Viscosity	Organo clays, Rhelogical modifiers
Fluid loss	Asphalt, Gilsonite, Lignite, Polymers
Alkalinity	Lime

2.1.3 Water-based mud

Water-based muds (WBM´s) contain a water phase instead of an oil phase and can be divided into freshwater muds, seawater muds and inhibitive muds (Strand 1998). Table 2 presents the main components of WBM´s and functions of the different components. An inhibitive WBM was used in this study.

Table 2: WBM´s – Main components and functions (SWACO 2011b). The table is edited.

WBM - Basics	
Water	Freshwater, Seawater, Salt saturated water
Density	Barite, $CaCO_3$, $FeCO_3$, Hematite, Illmenite
Viscosity	Biopolymers, Bentonite, CMC, PAC, Synthetic polymers
Fluid loss	Synthetic polymers, CMC, PAC, Starch, Bentonite, Lignites, Asphalt
pH-control	NaOH, MgO, $Ca(OH)_2$, Citric acid, $NaHCO_3$
Dispersant	Modified polyacrylates, Lignosulphonates
Inhibition	Glycols, Silicate, KCl, Gypsum
Other	Bactericides, Lubricants, Corrosion control, Polymer temperature stabilizers

Inhibitive WBM´s

Swelling of clay will be a problem due to the large amounts of water present in WBM. An inhibitive WBM will contain chemicals that prevent the mud from reacting with the clay and thus prevent swelling and formation instability. These chemicals may be polymers or salts. Polymers added to the WBM´s will inhibit clay swelling by adsorbing onto the clay particles or block formation pores and cracks. The polymer will act as a barrier between clay particles and water, which means less clay swelling. Salt added to the WBM will inhibit clay swelling by ion-exchange. The loosely bound Na^+ ions present on the clay particle surfaces will easily hydrate and thus the clay will swell and disperse. Salt ions present in the WBM´s such as K^+ or Ca^{2+} will replace the Na^+ ions due to their stronger binding energies. K^+ and Ca^{2+} will bind the clay surfaces more closely together and thus keep the water from entering the structure. Both polymers and salts have to be added continuously as they will be adsorbed onto the clay and used up. Types of inhibitive drilling fluids are $CaSO_4$, $Ca(OH)_2$, KCl, NaCl and lignosulphonate (Strand 1998). An inhibitive WBM known as Glydril (Figure 1) was used in this study.

GLYDRIL

Glydril is a WBM-system that uses polyglycol, KCl and polymers for inhibition. Polyglycol will inhibit some swelling by chemical adsorption, but the main inhibition mechanism is due to its cloud point. The cloud point is the temperature where polyglycol becomes insoluble, and at temperatures above this point polyglycol will form colloidal droplets and create a microemulsion. This microemulsion will inhibit swelling by adsorption and plug pores, and also by creating a thin and little porous filter-cake. Polyglycol have affinity for surfaces and can coat solids and other surfaces in the system. The type of polyglycol depends on well conditions/the desired cloud point (SWACO 1998). KCl will inhibit swelling by the K^+ ions that will exchange the Na^+ ions on the clay particle surfaces. In addition, polymers are added to encapsulate the clay particles and thus help prevent water intrusion (Strand 1998). Glydril provides a high degree of clay and shale inhibition, wellbore stability, fluid-loss control and lubricity, and offers qualities like good filter-cakes, less hole enlargement, reduced bit balling and increased ROP (SWACO 1998).

The use of WBM´s is increasing due to their environmental benefits and acceptance. WBM´s have previously had deficiencies compared to OBM´s, like poor inhibition, wellbore stability, ROP, lubricity and thermal stability, but with the help of chemical additives; WBM´s today are very efficient. Components and additives in these muds have minimal environmental and economical impacts, and in addition the WBM´s have high performance (Caenn et al. 2011).

2.2 Gas hydrates

Natural gas is found in porous rock in subsurface reservoirs often associated with crude oil. The gas is a mixture of hydrocarbons like methane, ethane, propane, iso-butane and pentane. Non-hydrocarbons can also be present in the mixture, like nitrogen, carbon dioxide and hydrogen sulfide. Methane is normally the largest constituent (about 85%) and ethane the next largest (about 5-10%) (Lundberg et al. 2009). When natural gas is produced it would normally be saturated with water vapor. This water may come from the formation (Carroll

2009) or it is present in the drilling fluid used during a drilling operation (Kim et al. 2007). Under certain conditions, many of the components in this gas mixture will form gas hydrates in combination with water. These components are typically gases that are gaseous in room temperature like methane and ethane. The gas hydrates are ice-like solids (Carroll 2009) that could cause a lot of different problems and hazards in drilling operations. They belong to a group of inclusion compounds known as clathrates (Sloan 2011), which consist of a host molecule and a guest molecule (or former). In this case the host is the water molecule and the former is a gas molecule from the gas mixture (Figure 3). The gas molecules will be entrapped in a network of water cages and hence these cages will be stabilized and solidify (Carroll 2009).

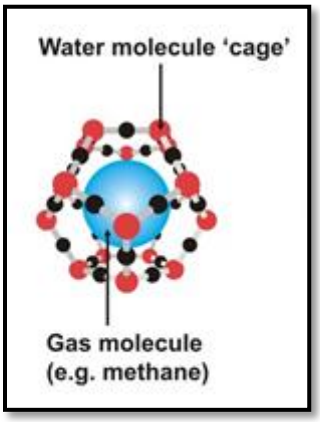


Figure 3: Gas hydrates consist of a host molecule (water) and a guest molecule (natural gas) (Hydrafact & University 2011). The figure is edited.

2.2.1 Hydrate formation

Water molecules are polar and have the ability to form hydrogen bonds. Hydrogen bonds are an electrostatic attraction due to the difference in electro-negativity between the hydrogen atoms and the oxygen atom. The water molecules will form hydrogen bonds between them due to a partial negative charge on the oxygen atom and positive partial charges on the hydrogen atoms. Gas hydrates are formed because of the water molecules ability to form hydrogen bonds. The hydrogen bonds will arrange the water molecules in three-dimensional cage-like structures in which formers can be entrapped under certain conditions due to Wan der Waals forces. Wan der Waals forces are attractive non-electrostatic forces between molecules.

These forces will occur between the formers and the water molecules and hence stabilize the structures. The former is not bound inside the cage and can therefore rotate (Carroll 2009). Certain conditions have to be present to enable the formation of gas hydrates. Gas hydrate formation is mainly dependent on the type and concentration of gas mixture, the amount of water present, the relationship between the temperature and pressure in the well, salinity of the system and time.

Usually the hydrates are formed at low temperatures and high pressures (Carroll 2009). The reason why the hydrates are dependent on pressure and temperature can simply be explained by le Chateliers principle and the displacement of the equilibrium (Equation I). When natural gas reacts with water/water vapor and forms hydrates, more hydrates will be produced due to an increase in pressure. A pressure increase will shift the equilibrium to the right because this will reduce the gas components in the mixture, hence more hydrates will be formed. Equally, a temperature decrease will shift the equilibrium to the right because gas hydrate formation is an exothermic reaction. The system will produce more heat and thus more solids to cancel out the temperature reduction.

Equation I: Water-Gas-Hydrate equilibrium.

$$\text{Water (g/l)} + \text{Gas (g)} \overset{\text{Exothermic reaction} \rightarrow}{\leftrightarrow} \text{Hydrates (s)}$$

This relationship can be shown in a pressure-temperature graph (Figure 4). The left side of the line shows the conditions where hydrates are formed, and the right side shows the conditions where no hydrates are formed. The line shows the hydrate equilibrium (Carroll 2009) (equilibrium between gas, water and hydrate) (Kelland et al. 2006) for a specific former or for a mixture of formers. These graphs can be made experimentally (Carroll 2009).

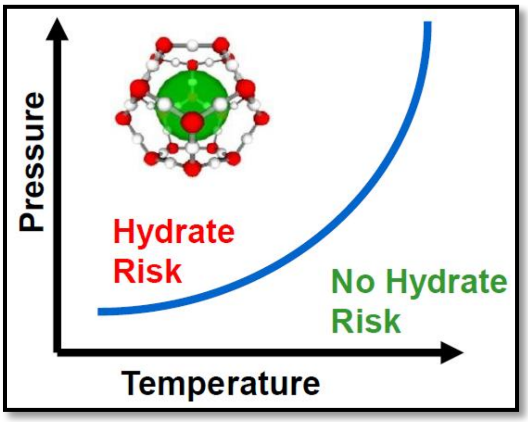


Figure 4: Hydrate formation is dependent on the temperature and pressure relationship. The equilibrium line (blue) is different depending on the type of former/mixture of formers (Hydrafact & University 2011).

An adequate amount of water and of course a former also has to be present. Normally water freezes at 0^{o}C, but hydrates will form at temperatures above this point if the pressure is sufficient. The water does not have to be in the liquid phase. Hydrates can form directly from the water in the gas phase to the solid phase because of the pressure present. Conditions that will enhance hydrate formation are turbulent flow and high fluid velocity.

Also the presence of nucleation sites like weld spots or particles like sand and silt will enhance hydrate formation. Free water will also have an effect due to nucleation sites on the water-gas interfaces (Carroll 2009).

Formation happens in two steps (Kim et al. 2007). Hydrates are usually formed at the gas-water interface, which starts with a thin film that grows fast on the water droplets. If an oil phase is present, hydrates will form at the oil-water interface due to water droplets emulsified in oil with dissolved gas molecules (Sloan 2011). This step is called nucleation and needs an induction time to create a critical size, and then the growth step begins (Kim et al. 2007). This step happens very rapidly. The droplets will due to capillary forces and movement eventually agglomerate, solidify and create a hydrate plug (Sloan 2011).

2.2.2 Types and formers

There are different classes of hydrates based on the water molecules arrangement in the crystal; type I, type II and type H (Figure 5) (Carroll 2009).

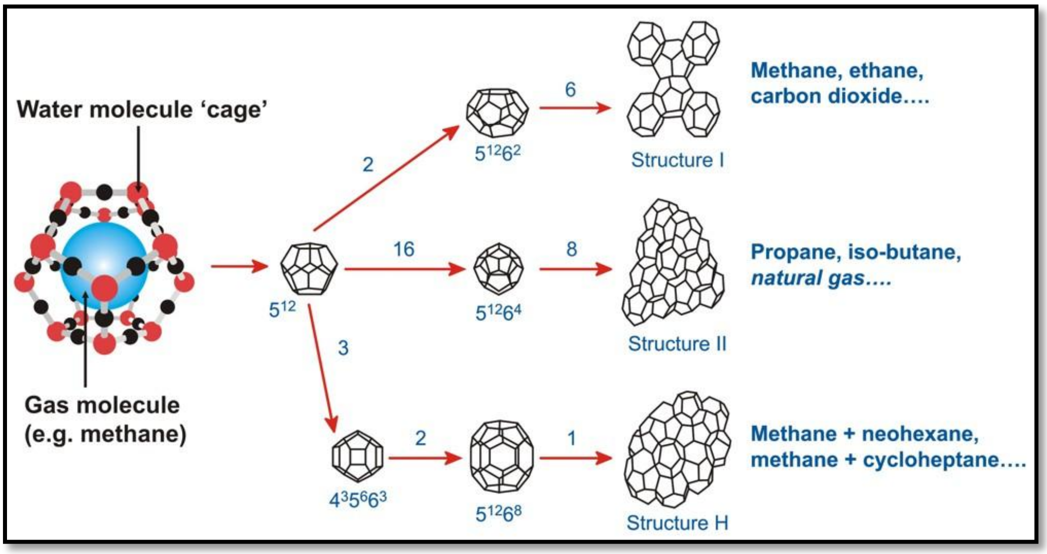


Figure 5: The different classes of gas hydrates (Hydrafact & University 2011).

Type I hydrates consist of small dodecahedron cages and large tetrakaidecahedron cages (Carroll 2009). The configuration consists of 46 water molecules. In this structure there are 2 small cages and 6 large cages (Hydrafact & University 2011). Typical formers are methane, hydrogen sulfide and carbon dioxide which can reside in both the small and the large cages, and ethane which can reside in the large cages only (Carroll 2009).

Type II hydrates consist of small dodecahedron cages and large hexakaidecahedron cages (Carroll 2009). The configuration consists of 136 water molecules. In this structure there are

16 small cages and 8 large cages (Hydrafact & University 2011). Typical formers are nitrogen which can reside in both the small and the large cages, and propane and iso-butane which can reside in the large cages only (Carroll 2009).

Type H hydrates are rarely found in natural gas. This type consists of small dodecahedron cages, medium irregular dodecahedron cages and large irregular icosahedron cages (Carroll 2009). The configuration consists of 34 water molecules. In this structure there are 3 small cages, 2 medium cages and 1 large cage (Hydrafact & University 2011). Two formers need to be present to make type H hydrates stable because they always form double hydrates. Smaller formers are needed to fill the small and medium cages, and bigger formers are needed to fill the large ones. A typical small former is methane, whilst a large former may be molecules like methylcyclohexane and cyclooctane (Carroll 2009). Recent research shows that type H hydrates can form at higher temperatures than structures I and II. This may have to be taken under consideration because hydrates can form at other conditions than before thought (Executive 1997).

There is no need for all of the cages to be filled with a former to make the hydrate stable. How much former needed is dependent on the pressure and temperature conditions. Some formers like ethane, propane and isobutene are not dependent on temperature and pressure because they only reside in large cages (Carroll 2009).

Hydrates are only formed if the diameter of the gas molecules are greater than 3,8 Å. Type I and type II hydrates are only formed if the gas molecules are less than 7,0 Å. Type H hydrates are greater than this value and have a maximum of 9,0 Å. In addition, water cages will never form hydrates with water soluble formers. The former can be present in gaseous or liquid phase (Carroll 2009). There is restriction on the former size because hydrogen bond deviation will present non-ideal cages (Chandragupthan 2011).

Oil and gas operations usually deal with gas mixtures, and normally type II hydrates will be the most abundant due to the presence of large gas molecules (Carroll 2009; Sloan 2011). Some formers have the unusual behavior of forming another type of hydrate than expected. Methane and ethane for example which is both type I will form type II if they are in a mix. A mixture of type I and type II formers will usually form the more thermodynamically stable type, which means the type where the free energy is as low as possible (Carroll 2009).

2.2.3 Hydrates in drilling operations

Formation of hydrate plugs is an increasing concern in drilling operations (Figure 6). Today drilling is carried out in deeper waters, the temperatures will thus be lower and the pressures will be higher. Hence the probability of hydrate formation is higher. A major issue of concern is prediction, control and removal of plugs. Plugs represent great health risks, costs and environmental hazards. Plugs may detach and launch during pressure reduction, damage the equipment and several types and large amounts chemicals are required for the removal (Executive 1997).

Figure 6: A gas hydrate plug (Hydrafact & University 2011).

Plugs can form wherever water and gas are present together with the right temperature and pressure. Temporary operations like start-up or restart after an operational shut-in will cool the system and are typical situations where plugs can be formed. Also abnormal operations like malfunction of inhibitor injection or cooling of a flow across a valve can cause plugging. Plugs can form in many locations in an offshore system (Sloan 2011). The wellhead is commonly outside the hydrate region (Hydrafact & University 2011). Typically plugs or blockages are found in the flow-line, especially where there's a slope or irregularity which causes an accumulation. Plugs are also formed in the riser and in the Christmas three due to their many valves (Sloan 2011). BOPs, choke lines and kill lines are cooled due to depressurized flow and plugs can also be found here. The drill-string and the casings could also be affected when there is no rotation and thus heat production. The growth of hydrates in the equipment will affect both rotation and circulation. The lack of proper equipment function will make the process less efficient or in worst case it will stop, and may lead to high risk situations. For example if the BOP isn't working properly, this may cause a blow-out (Executive 1997).

Hydrates also form in drilling fluid systems. Especially there's a greater risk when using water-based fluids than oil-based fluids because of the larger amount of water present.

The reason why oil-based fluids are more inhibitive is because the water droplets are emulsified in oil (Sloan 2011). When hydrates form they will alter the properties of the drilling fluid. This would affect the drilling fluids rheological properties and affect the flow and circulation in the system (Kim et al. 2007). The hydrate formation will extract water from the drilling fluid, form solids and thus change its viscosity (Executive 1997). Salt may also precipitate due to the water removal (Hydrafact & University 2011). As described earlier, the drilling fluid has to work properly due to its essential role in controlling well conditions during a drilling operation.

2.2.4 Gas hydrate control

There are several methods that have been frequently used to prevent or remove hydrate plugs, but some of these methods are often impractical, ineffective, expensive and dangerous (Patel et al.). Hydrates may be prevented by controlling the pressure and the temperature in the system or by injecting chemicals during the operation. Controlling the pressure and temperature means operating at conditions outside the hydrate forming region, which may be difficult in deep water environments. Injection chemicals like methanol, ethanol and glycols (as monoethylene glycol (MEG)) may inhibit hydrate formation if added to the system. The chemicals are pumped into the system through a line and mixed with the produced fluids.

If it comes to a point where plugs already are formed, the operation has to stop and the plugs must be removed. These plugs can be removed by reducing the pressure, by increasing the temperature, mechanically or by injecting chemicals onto the plug. By reducing the pressure, the plug will dissociate and melt (Sloan 2011). In some cases this may be fatal because the plug may detach and launch (Kim et al. 2007). Temperature increase can be done by heating the plug to a point over its equilibrium point for example by the circulation of warm mud or heated brines (Sloan 2011). Reactive chemicals that generate heat could also be used to dissociate plugs (Sloan & Koh 2008). Mechanically means using different tools to scrape out and remove the solids. Chemicals may also be injected after the plug is formed, but blockages may make it difficult to get the chemicals next to the plug.

Plugs have been proven to be porous and permeable, but in gas systems the gas between the plug and the injection point will hinder the inhibitors in flowing down to the plug. Chemicals will in this case be used in large volumes and this will be very expensive, especially if the plug is far from the injection point (Sloan 2011).

Clearly, the best way will be prevention rather than removal. This would be the more cost-efficient, time saving and risk free method as new inhibition methods gets more effective, practical, environmental friendly and economical. The use of chemicals called thermodynamic hydrate inhibitors (THI´s) offers many of these qualities and is used in many operations today. Recently, great emphasis has been put on the use of low-dosage hydrate inhibitors (LDHI´s) which are a new type of inhibitors. These may present even more of the desired qualities. In addition, a more efficient method will be to add these inhibitors into the drilling fluids before circulation, as the drilling fluid and the formation are the sources of water in the system. This method will rapidly get the inhibitors in touch with the water, less amounts of chemicals will be used and the operation can be performed under deepwater conditions if the inhibitors are efficient.

Some constituents of drilling fluids are known to be hydrate inhibitors and some to be hydrate promoters (Executive 1997). Publications involving gas hydrate formation in drilling fluids are few, and very little equipment is designed for tests (Kim et al. 2007).

2.3 Chemical inhibitors

There are generally three classes of chemical inhibitors which could be added to the drilling fluids for hydrate plug prevention.

The first class is the thermodynamic hydrate inhibitors (THI´s). These are the more conventional ones and are commonly used in operations today. They are frequently utilized because their mechanisms are well-known, also they are predictable and effective (Chandragupthan 2011). The drawback of using THI´s is that these chemicals are dependent on specific and stable conditions (Patel et al.). In addition, relatively high concentrations have to be used (Chandragupthan 2011). Drilling operations are now performed in deeper waters than before which means harsher conditions. The production rates are also increasing. Hence, there is a need for more cost-effective and diverse inhibitors (Patel et al.).

The low-dosage hydrate inhibitors (LDHI´s) are divided into kinetic hydrate inhibitors (KHI´s) and anti-agglomerants (AA´s) due to their chemical structures and properties. These inhibitors have received much attention the last 15-20 years (Kelland et al. 2006). The LDHI´s are added at much lower concentrations than the THI´s. Lower dosages will consequently reduce costs (Patel et al.) not only on chemicals, but also due to fewer deliveries and smaller storage requirements (Nalco 2011). There will also be environmental benefits as smaller amounts of chemicals are used (Pickering et al. 2001), and they will be more practical to use.

The LDHI´s are mainly non-toxic, thus handling, storage and the environment will be safe. They can also be applied to much bigger water cuts than the THI´s (Nalco 2011).

Today, LDHI´s have been used in over one hundred operations all over the world and their emphasis is getting greater every day. As their mechanisms and the technology is explored and recognized, these inhibitors will be more frequently used (Kelland 2012). In gas-based systems LDHI´s have had many successful applications (Pickering et al. 2001). A large amount of information and research about the chemistry of these inhibitors is kept confidential; hence information is difficult to find (Kelland 2006).

2.3.1 Thermodynamic inhibitors

The use of THI´s is the most common hydrate inhibition method today. THI´s are known as anti-freezes (Kelland 2012) and are primarily alcohols and naturally inorganic salts (Pickering et al. 2001). Alcohols commonly used are methanol, ethanol and glycols like MEG (Kelland 2012). NaCl, KCl and $CaCl_2$ are examples of salts frequently used (Chandragupthan 2011).

The subcooling (ΔT) is an essential term when dealing with hydrate inhibition. Subcooling is a measurement of the driving force for hydrate formation (24) at a given temperature and pressure with a specific gas mixture present (Kelland et al. 2006). The operating point for a system can be shown in a pressure-temperature graph together with the equilibrium curve for the specific gas mixture (Figure 7) (Kelland 2012). The operating point is the minimum temperature and pressure present in the well fluids during the operation (Kelland 2012). The subcooling (ΔT) is the distance on the temperature axis between the operating point and the equilibrium curve (Kelland et al. 2006). The graph also shows what amount of pressure reduction or temperature increase that has to be applied to the system to prevent or remove the hydrates, as the right side of the equilibrium curve is the hydrate free region.

The additional subcooling in this study is calculated as the average hydrate formation value for the base fluid *minus* the average hydrate formation temperature of the different samples.

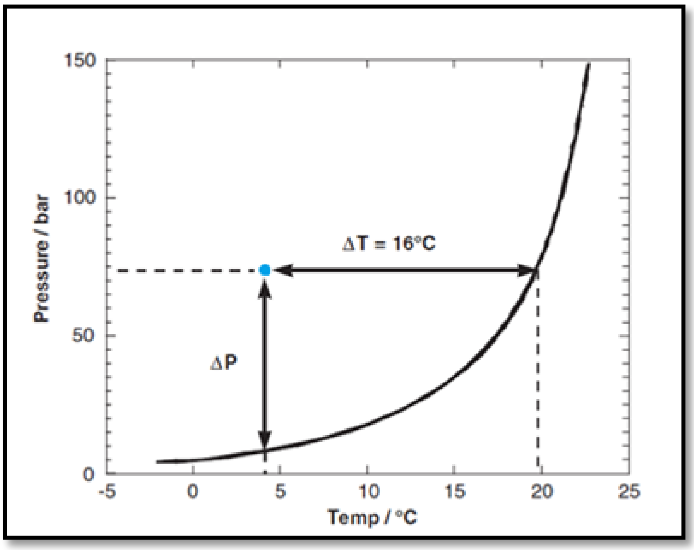


Figure 7: Operating point (blue) at 4^{O}C and 75 bar, hence a subcooling of 16^{o}C for a specific gas mixture (Kelland et al. 2006). The figure is edited.

THI´s work by shifting the hydrate equilibrium curve to the left (Figure 8). In this way the hydrates will form at lower temperatures and higher pressures than without the inhibitor present. If the curve shifts past the operation point, the operation will take place outside the hydrate forming region and in principle no hydrates will be formed (Patel et al.).

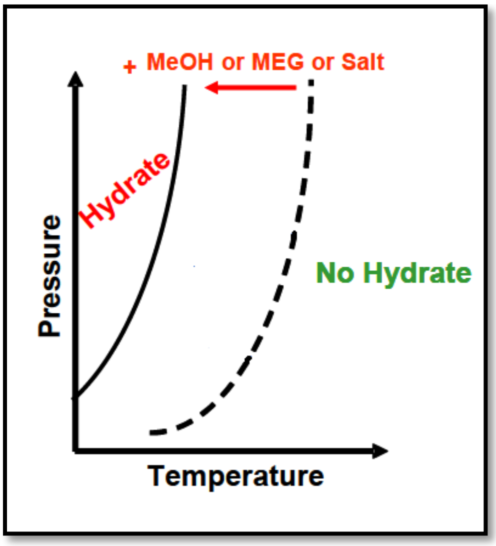


Figure 8: THI´s shifts the hydrate equilibrium curve to the left (Hydrafact & University 2011). The figure is edited.

The effectiveness of THI´s depends on the subcooling. If the subcooling increases, the concentration (wt. %) of THI´s has to be increased because the operation point will be further to the left. The higher the concentration, the further the equilibrium curve will shift to the left. THI´s are also very sensitive to any small changes in the subcooling during the operation (Patel et al.).

THI´s inhibit gas hydrate formation by decreasing the chemical potential (µ) of the water molecules present. In this way the equilibrium will shift to the left (Equation II), and hence the system needs bigger strain to form hydrates (Chandragupthan 2011).

Equation II: Chemical potential equilibrium (Chandragupthan 2011).

$$\begin{array}{ccc} \text{Water} + \text{Gas} & \leftrightarrow & \text{Hydrate} \\ \mu_{\text{water}} + \mu_{\text{gas}} & \leftrightarrow & \mu_{\text{hydrate}} \end{array}$$

The chemical potential is a measurement of stability. A substance with high chemical potential has a higher tendency to react and move from one phase to another in order to lower the Gibbs free energy. The Gibbs free energy tells if a reaction is spontaneous or not. When the THI´s reduce the water molecules potential, the water molecules will be less reactive and the tendency to form cages and thus hydrates, will be reduced. The hydrate-forming reaction will be less spontaneous.

The potential of the water molecules is reduced due to the chemical structures of the THI´s (Sloan 2011).

Methanol and MEG (Figure 9) both have oxygen atoms which each has two non-bonded pairs of electrons. These atoms have a partially negative charge, which will make hydrogen bonds with the partially positive charges on the hydrogen atoms on the water molecules. In the same fashion, the hydrogen atoms on the inhibitor will make hydrogen bonds with the oxygen atoms on the water molecules. These are the same type of bonds as in the water cages. Hydrogen bonding between the inhibitor and the water molecules will prevent the water molecules from forming hydrogen bonds with each other and thus forming cages. The inhibitor will compete for hydrogen bonds and thereby reduce the amount of water used for hydrates. This will keep some of the water in the liquid phase. To prevent more water from reacting, higher concentrations of inhibitor is needed. This means that lower temperatures and higher pressures are needed to form hydrates because of less uninhibited water (Sloan 2011). The degree of inhibition depends on the THI structure; the longer the carbon chain, the less inhibition. In addition, inhibition is increased the more hydroxyl groups that is present on the carbon chain due to more hydrogen bonding with water molecules. If two alcohols have the same carbon chain length, the more inhibitive will be the one with more hydroxyl groups. MEG for instance, has two hydroxyl groups. The degree of inhibition is primarily dependent on carbon chain length and secondarily on the hydroxyl groups; hence methanol will be the more efficient inhibitor (Chandragupthan 2011).

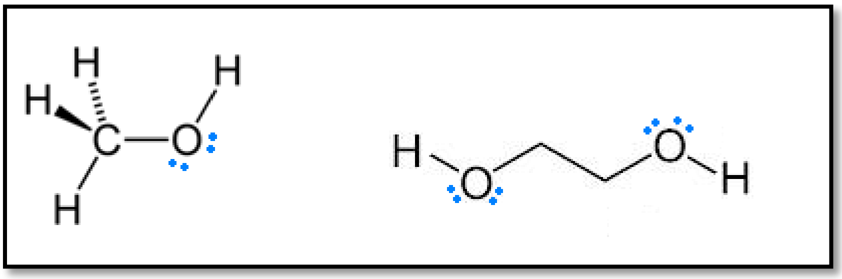


Figure 9: Chemical structures of Methanol (left) and MEG (right). The alcohols have non-bonded pairs of electrons (blue) which form hydrogen bonds with water.

Salts also have the ability to inhibit hydrate formation. Salts are ions when dissolved in water due to the partial charges on the water molecules which attract the opposite charges on the ions (Figure 10). Because the ions will be attracted to the water molecules, less water molecules will be able to participate in cage formation. The salts will only inhibit gas hydrates to a certain extent and it is rarely sufficient to use salts alone. This is due to the extreme conditions in the cold deep waters (Son & Wallace 2000); when the temperatures are low, salts will have less solubility which will set a certain limit. As for the alcohols, the concentration (wt. %) of the salts also needs to be increased to shift the equilibrium curve further to the left. Salt has more impact on the shift than the alcohols, and on a weight percent basis salts are the more effective inhibitor of the two (Bai 2005). This is probably due to the strength of ion-dipole bonding compared to hydrogen bonding.

NaCl is one of the most inhibitive salts, while KCl is not very effective compared to NaCl. $CaCl_2$ is very effective in high concentrations (Power et al. 2003). Salts from the formation could also act as THI´s (Pickering et al. 2001). Table 3 shows some advantages and disadvantages of some types of THI´s.

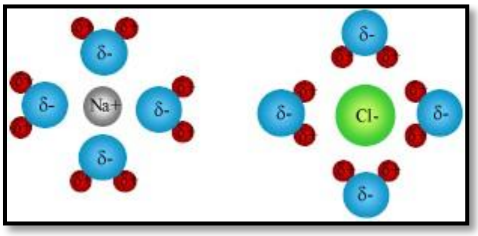


Figure 10: Ionic bonds are broken and the ions are attracted towards the water molecules' partial charges (Carpi 2003).

Table 3: Comparison of some THI´s (Bai 2005; Chandragupthan 2011; Power et al. 2003; Sloan 2011; Son & Wallace 2000).

THI	**Advantages**	**Disadvantages**
Methanol	Effective - moves hydrate equilibrium more than MEG on weight percent basis	Low molecular mass: easily vaporized into gas phase - losses and escape from system due to increased temperatures
	Less expensive than MEG	Low flash point: highly flammable and explosive - presents health risks
	Less viscous than MEG	Toxic - presents health risks due to storage and handling, environmental hazards - environmental restrictions
	Less likely to cause salt precipitation than MEG	Catalyst: Can catalyze unwanted chemical reactions - e.g. interference with corrosion inhibitors
MEG	Higher molecular mass: non-volatile - neglible amounts vaporized out of the system	High viscosity
	Low gas and condensate solubility	Can cause salt precipitation - hence corrosion and fouling problems
		Dispersive effects when drilling into certain formations
		Toxic - presents health risks due to storage and handling, environmental hazards
		Expensive
		Less effective than methanol
Salts	The most effective THI´s	Solubility limitations in cold deep water environments
	NaCl and KCl: no toxic effects	$CaCl_2$ may have some environmental and technical restrictions

2.3.2 Low dosage hydrate inhibitors

LDHI´s are normally dosed at 1-3 wt. % (Kelland 2012) based on the water present in the drilling fluid while THI´s have to be dosed 20 to 60 times higher (Kelland 2012). Usually, the active concentration of the LDHI is 20-40%, thus the active dose is often in the range of 0,2-1,0 wt.% (Kelland 2012). As described, there will be many benefits by adding LDHI´s to the drilling fluid instead of or in addition to the THI´s. The lower costs associated with the LDHI´s together with their non-toxic nature will make them the novel and modern type of inhibitors used in drilling operations.

The LDHI´s can be divided into two classes; KHI´s and AA´s which are water-soluble polymers and surfactants respectively. These inhibitors prevent hydrate formation by different mechanisms and can be effective under different conditions than the THI´s (Kelland 2012).

2.3.2.1 Kinetic hydrate inhibitors

KHI´s are low molecular weight polymers (Sloan 2011) of fatty acids, mixtures of fatty alcohols and amines (Chandragupthan 2011). They are composed of a polyethylene strand with lactam rings (Sloan 2011). Examples are Poly-N-Vinyl-N-Caprolactam (PVCap) and Poly-N-Vinylpyrrolidone (PVP) which both are poly-N-vinyllactams (Figure 11). Typically the polymers contain polar amide groups (-$RCONH_2$) or hydroxyl groups (-OH) and a non polar ethylene strand. Good KHI performance requires at least 8-10 repeat units (Mw of at least 1200-2000). If the chain has fewer repeat units, performance will drop drastically. Some non-polymeric molecules could also potentially be used as KHI´s (Kelland 2012). They are poor inhibitors on their own, but can work as synergists. Low molecular weight polymers such as PVCap with synergists have shown to be the best KHI´s (Kelland 2006). PVCap has shown to be more effective than PVP (Dirdal et al. 2011). An important criterion is that the polymers have to be water-soluble and adsorb well to polar surfaces (Chandragupthan 2011). The KHI´s have to be added to a carrier solvent because of their low concentrations (Sloan 2011), in this case a drilling fluid.

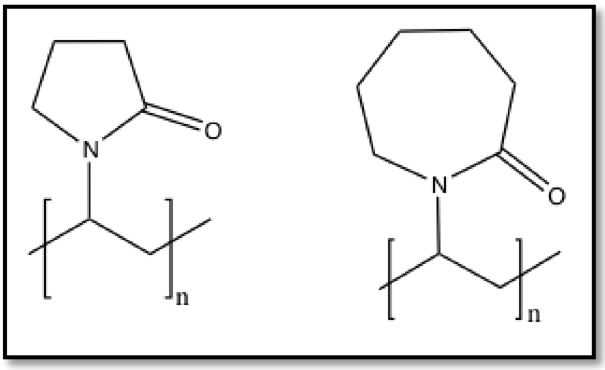


Figure 11: Chemical structures of PVP (left) and PVCap (right) (Warwick 2012). The figure is edited.

In contrast to THI´s which alter the thermodynamics in the system, KHI´s will alter the kinetics (Pickering et al. 2001). KHI´s are time dependent unlike THI´s. Instead of preventing the gas hydrate formation from happening, KHI´s mechanism work by shifting the equilibrium conditions and delay the hydrate formation for a period of time (Figure 12). This means that hydrates will form at lower temperatures and higher pressures (provide subcooling), and in addition give the system some extra time before the first hydrates starts forming.

This delay period is known as the induction time, is mainly dependent on the subcooling and will be shorter the greater the subcooling. Some classes of KHI´s have in addition to these features in some cases been proven to inhibit crystal growth (Kelland 2006), reduce the rate of formation and limit crystal size (Power et al. 2003).

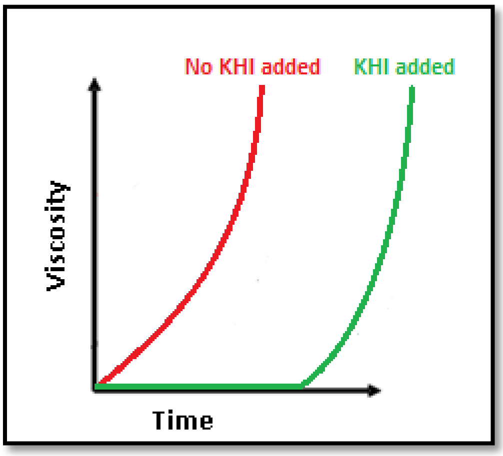


Figure 12: The addition of KHI delays the hydrate formation. Here shown as a function of viscosity.

Other factors that affect KHI´s performance are the composition of the gas present (Kelland 2006), the composition of the well fluids (Kelland 2012), salinity in the system, mixing (Kelland 2006) and the amount of water present (Kelland 2012). A minimum concentration has to be used for the KHI´s to have sufficient performance. Further increase in concentration may have various effects depending on the type of polymer (Dirdal et al. 2011). KHI´s have shown to be very effective at high pressures, especially with THI´s present (Kelland 2012). Their efficiency is rated based on their degree of subcooling (Sloan 2011), and they are commonly limited to a subcooling less than 10-12^{0}C. At subcoolings higher than this, very short induction times will be provided (Kelland 2012). Some KHI´s have managed up to 15^{0}C subcooling or higher, but are not commercially available (Kelland 2006).

The mechanisms for KHI hydrate inhibition are still not fully understood (Kelland 2006). One mechanism could be that KHI´s delay the formation by hindering the nucleation. By hindering the nucleation, KHI´s will prevent the gas hydrates from reaching their critical size and thus delay the growth phase. At their critical size the Gibbs free energy will become negative and the formation will happen spontaneously and rapidly. Since the formation starts at the water/gas interface, it's important for the KHI´s to be water soluble. If possible, higher concentrations at the interface are desired. It's thought that the amide and hydroxyl groups in the KHI´s will bind to the ice-crystal nucleation structure thus preventing growth. The groups have to be spaced in a specific manner to fit into and align with the ice structure´s surface. The binding mechanism is suggested to be either hydrogen bonding or due to hydrophobic interactions. Another possible mechanism it's thought that KHI´s work by is that they will absorb onto the surfaces of growing hydrates which have reached their critical size. This absorption will delay further growth (Kelland 2012) through steric hindrance (Power et al. 2003) and also by distorting the hydrate cages (Kelland 2012). The binding mechanism may be due to the groups on the KHI´s which can imitate formers and thus enter the cages. Polymers with similar sizes as the cage spaces seem to be the most effective (Kelland 2012). The ring-structures will act as "pseudo guests" in the cages on the hydrate surfaces, and act as an anchor for the polyethylene polymer. Lactam groups for example fit well into large cages of structure II. The occupation of the polymer in the hydrate cages will provide a barrier that has to be broken for the gas to enter and hence cause hydrate formation (Sloan 2011). The polymer will be bound to the cages due to hydrogen bonding. A third probable mechanism is that the polymers may be adsorbed to surfaces like particles or weld spots. This would reduce the nucleation sites in the system and thus reduce hydrate formation (Kelland 2012). Table 4 shows some advantages and disadvantages by using KHI´s.

Table 4: KHI advantages and disadvantages (Chandragupthan 2011; Kelland 2012).

Advantages	**Disadvantages**
Generally non-toxic and environmental friendly	May have limited biodegradebility in seawater, intermediates may be toxic during degradation, bio-accumulation may present a problem - need for greener KHI´s
Can be used in multiphase-, gas- and condensate systems - mostly tested in gas systems	May interfere with other substances in the system, e.g. corrosion inhibitors
Provide time in addition to subcooling	
Lower concentrations needed than for the THI´s	Expensive, epecially at high water cuts - normally used in gas systems with low watercuts
	Limited reseach in oil systems
	Mechanisms are not fully understood
	Limited subcooling

2.3.2.2 Anti-agglomerants

AA´s are classes of surfactants (Kelland 2012) which mean they are surface active agents (18). Typically AA´s are long molecules of quaternary ammonium salts (Sloan 2011). Other classes off AA´s could also be used, but they are not commercially available (Kelland et al. 2009). A quaternary ammonium salt is a salt where the cation is an ammonium ion where the hydrogen atoms could be replaced by alkyl- or aryl groups, and an anion (Figure 13)

(OChemPal 2009). Normally two or more butyl or pentyl groups are replacing the hydrogen atoms (Kelland et al. 2009).

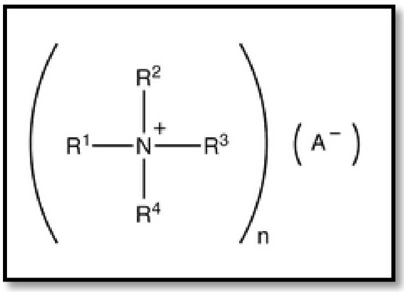


Figure 13: General structural formula of quaternary ammonium salts, n is a positive number of repeats. R could be hydrogen, alkyl groups or aryl groups (OChemPal 2009).

Agglomeration of the hydrate particles due to capillary forces is the major factor for plug formation (Sloan 2011) (Figure 14). AA´s prevent plug formation by allowing hydrates to form (Kelland 2006), but will attach to their surfaces and thus prevent them from agglomerating (Kelland 2012). This means that the hydrates can be transported out of the system as a slurry. AA´s weakness is that they only work in a continuous oil phase and therefore only at low water cuts (Pickering et al. 2001).

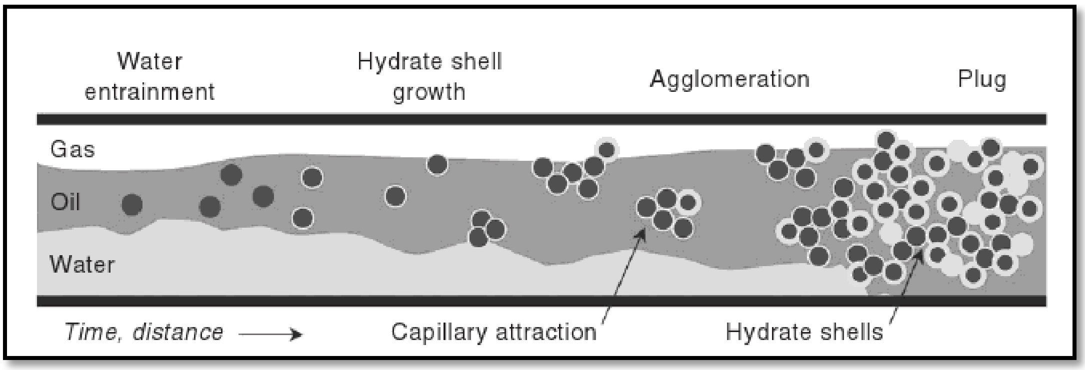


Figure 14: Hydrate plugs form because of agglomeration (Sloan 2011).

In a continuous oil phase, the water will be suspended in droplets. Free water within and between the droplets will cause the capillary attractions. The emulsified water droplets will grow hydrate shells on their interfaces and shrink inwards to a solid hydrate. Normally one end of the long salt molecule will have affinity for the hydrate (hydrophilic) and the other affinity for oil (hydrophobic). When the salt molecule is attached, the hydrate surfaces will repel other hydrates due to the hydrophobic part which is pointing outwards. Nucleation sites on hydrated droplets will also be removed. The hydrates will consequently be suspended, agglomeration into plugs will be prevented and thus the flow in the system will not be compromised (Sloan 2011). AA´s are generally dependent on the same factors as the

KHI´s, but to a smaller extent (Kelland 2006). Table 5 shows some advantages and disadvantages by using AA´s.

Table 5: AA advantages and disadvantages (Chandragupthan 2011; Kelland 2006; Kelland 2012; Pickering et al. 2001; Sloan 2011).

Advantages	Disadvantages
Provide higher subcoolings than the KHI´s - for systems with high subcoolings AA´s may be the only LDHI alternative	Require a continous oil phase - no effect in gas systems
Not as temperature- and pressure dependent as the KHI´s - more suitable for deep water conditions	Require low water cuts - lower than for THI´s and KHI´s - water cuts of over 50% will make the slurry too viscous to circulate
Longer system residence time than KHI´s	Effectiveness compared to KHI´s uncertain due to less experience and predictive models
Can be used in multiphase-, condensate- and oil systems	
Generally non-toxic and environmental friendly Less expensive than the KHI´s	

KHI´s are the more commonly used LDHI´s in field applications, but the use of AA´s is increasing rapidly (Kelland 2006). Some KHI´s may have anti-agglomerate behavior (Power et al. 2003) and some AA´s may display kinetic hydrate inhibitor effects (Pickering et al. 2001).

2.3.3 Surfactants

Surfactants are organic compounds which have the ability to adsorb onto surfaces and interfaces. Three typical features characterize a surfactant: 1) The hydrocarbon chain has at least one polar and one non-polar group, 2) The substance is surface active and 3) The substances will interact with themselves to self-assembly into organized patterns in liquids. Hence, surfactants have the ability to both adsorb and aggregate. The surfactants have two main structures: polar/hydrophilic heads, and non-polar/hydrophobic tails which make them soluble in many types of solvents. If a surfactant is added to an aqueous liquid, it will adsorb to air/water- and solid/water interfaces. The polar groups will face towards the liquid and form a hydrophilic layer, while the non-polar groups will face towards the air or solid and make a hydrophobic interior (Figure 15). This is a dynamic and rapid process where molecules arrive and leave the surfaces constantly (Farn 2006).

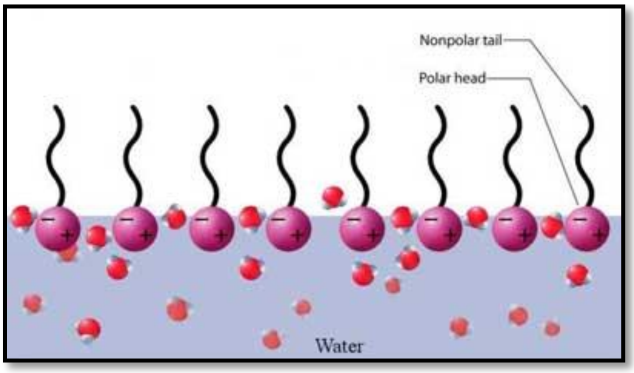


Figure 15: How surfactant molecules will arrange in an aqueous liquid (Ltd 2011).

The surfactants also have the ability to arrange themselves in a fashion that will reduce the hydrophobic groups' contact with water (Farn, 2006) and thus minimize the solutions Gibbs free energy (Ramaswamy et al. 2011) . They will self-assemble and aggregate in structures called micelles. The hydrophilic groups will then face towards the aqueous phase and the hydrophobic groups face towards a center. Micelles have different configurations, typically they are spherical, cylindrical or lamellar (Figure 16). Their shapes are dependent on the concentration, temperature, pH and if there is salt present. Micelles start forming at a relatively low concentration of the surfactant, known as the CMC. Different surfactants will have different CMC values. CMC is the concentration where the adsorbtion is complete and the surface activity is maximized. Micelles have no surface activity. Micellization is also a dynamic process (Farn 2006).

The properties of the surfactants make them able to solubilize and emulsify molecules or substances in an aqueous solution. Addition of surfactants will give both the interfaces and the solution different properties (Farn 2006).

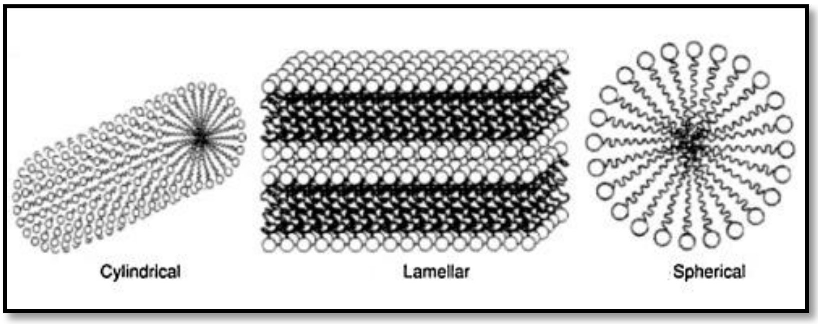


Figure 16: Micelles have different configurations depending on the conditions present in the fluid (Farn 2006). The figure is edited.

The properties of the surfactants depend on the type of hydrophobic and hydrophilic groups, thus many different combinations and properties can be obtained. In addition the molecules can have one head and one tail, one head and two tails, two heads combined with one tail, two heads combined together with an organic spacer molecule or several heads combined together with covalent bonds (Farn 2006).

The hydrophilic part classifies the surfactant as anionic, cationic, non-ionic or amphoteric. In aqueous solutions anionic and cationic surfactants will dissociate into ions. The result will be anionic and cationic heads, and cationic and anionic tails respectively. Since the heads of cationic surfactants are positively charged they would have the ability to adsorb to negatively charged surfaces such as clay. Non-ionic surfactants will not dissociate in aqueous solution and their heads will have no charge. The heads of amphoteric surfactants may be positively charged, negatively charged or have both charges (zwitterions) depending on the pH of the solution. In an acidic and alkaline environment they will be cations and anions respectively. In a neutral environment they will be zwitterions. Typical hydrophilic and hydrophobic groups are presented in table 6 and 7 respectively (Farn 2006).

Table 6: Typical surfactant hydrophilic groups (Farn 2006). The table is edited.

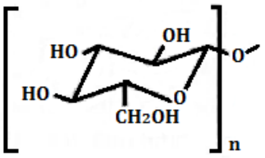
Ionic type	**Example**	**Structure**
Anionic	Sulphate	$-OSO_2O^-$
	Sulphonate	$-SO_2O^-$
	Ether sulphate	$-(OCH_2CH_2)_nOSO_2O^-$
	Ether phosphate	$-(CH_2CH_2O)_nP(O)O^-$
	Ether carboxylate	$-(CH_2CH_2O)_nCO_2^-$
	Carboxylate	$-C(O)O^-$
Cationic	Primary ammonium	$-N^+H_3$
	Secondary ammonium	$-N^+(R)H_2$
	Tertiary ammonium	$-N^+(R)_2H$
	Quaternary ammonium	$-N^+(R)_3$
Amphoteric	Amine oxide	$-N^+(R)_3O^-$
	Betaine	$-N^+(R)_3(CH_2)_nC(O)O^-$
	Aminocarboxylates	$-N^+H(R)_2(CH_2)_nC(O)O^-$
Non-ionic	Polyoxyethylene (an ethoxylate)	$-(OCH_2CH_2)_nOH$
	Acetylenic	$-CH(OH)C{\equiv}CH(OH)-$
	Monoethanolamine	$-NHCH_2CH_2OH$
	Diethanolamine	$-N(CH_2CH_2OH)_2$
	Polyglycoside	

Table 7: Typical surfactant hydrophobic groups (Farn 2006). The table is edited.

Group	Example	Structure
Alkylbenzene	Linear dodecyl-benzene	$CH_3(CH_2)_5CH(C_6H_4)(CH_2)_4CH_3$[a]
Linear alkyl[b] (saturated)	n-dodecyl	$CH_3(CH_2)_{10}CH_2$-
Branched alkyl[b] (saturated)	2-ethyl hexyl	$CH_3(CH_2)_3CH$-CH_2-(CH_2CH_3)
Linear alkyl[b] (unsaturated)	Oleyl	(cis-)$CH_3(CH_2)_7$=$CH(CH_2)CH_2$-
Alkylphenyl (branched)	Nonylphenyl	$C_9H_{19(\text{branched isomers})}C_6H_4$-
Polyoxypropylene		-$[OCH_2CH(CH_3)]_n$-
Polysiloxane		$(CH_3)_3Si[OSi(CH_3)]_nOSi(CH_3)_3$

[a] Alkylbenzene has a linear alkyl chain with, in the case of dodecyl, the phenyl group distributed between the second and sixth positions on the aliphatic chain. The C_6 isomer is illustrated above.

[b] Alkyl groups, whether linear, branched/saturated or unsaturated, are usually within the C_8 to C_{18} chain length range.

A surfactant should be able to adsorb onto surfaces and interfaces at relatively low concentrations. This will lower the surface- and interfacial tensions on the molecules and particles present. Hence the surfactants will reduce their ability to react by reducing their free energy. For a surfactant to be surface active it needs at least 8 carbon atoms at their hydrophobic tail, but maximum effect is when there are 10-18 carbon atoms present. The longer chain of carbon atoms, the more the solubility will be reduced. A 19 carbon chain or longer will make the surfactant insoluble (Farn 2006).

Surfactants can be of natural or synthetic origin and have limited applications. They can be used in agriculture, cosmetics, detergents, household products, food, petroleum plastics and textiles. Some of their surface active properties are wetting, foaming, emulsification, dispersion, solubility, lubricity and viscosity modification (Farn 2006). In drilling fluids they are commonly used for foaming, emulsification and dispersion (Schramm 2000). The petroleum industry is a large consumer of surfactants (Farn 2006). Surfactants may be both toxic and bio-accumulative, depending on the type. This needs to be taken into account when used as oil field chemicals.

2.3.4 Combination of inhibitors and WBM compatibility

Even the best WBM´s today are not adequate to prevent hydrate formation in harsh deepwater environments with high subcooling and high pressures (Mønig et al. 2008).

Although cheap salts are the most effective THI´s, sufficient amounts of salts to inhibit hydrate formation will make the mud weight too high for the use as low-density fluid in deep water applications. This will limit the use of salt in the drilling fluid, in addition to salts' low solubility at cold temperatures. To achieve acceptable THI inhibition, the mud must therefore be boosted by the addition of large amounts of expensive glycols. The use of this combination will thus make a very expensive drilling fluid (Power et al. 2003) and it will have a limited ability to prevent hydrate formation. Another problem will be the decreased solubility of the salts when increasing the amounts of glycols, hence compromises needs to be made (Mønig et al. 2008).

KHI´s and THI´s are often combined in deepwater WBM´s to increase performance. KHI´s will give the drilling fluid the extra inhibition needed, make a cheaper drilling fluid due to the KHI´s lower concentrations and reasonable price, and also limit the mud weight increase. Gas hydrate tests for drilling fluids have to be performed to provide the optimal concentrations of the combination of THI´s and KHI´s.

Important features of the KHI´s used in drilling fluids are that they have to be soluble in the aqueous phase, particularly at the operation temperatures. The KHI´s must have sufficiently high cloud points as they precipitate and thus break their hydrogen bonding with the water molecules over this point. This will put off their inhibitive effect, thus the KHI´s cloud point should be over the circulation temperature. Another feature that has to be taken into account is that the KHI´s cloud points will decrease with increasing salinity (Mønig et al. 2008).

2.3.5 Surfactants and their effect on gas hydrate formation

Surfactants may act as synergists to give the KHI´s better performance as the KHI´s used today have limited subcooling. These compounds may modify surfaces of particles in the drilling fluid, remove some nucleation sites and hence reduce hydrate formation. The surfactants may also have antagonistic effects depending on their chemical reactions with the different substances present in the drilling fluid. A small amount of literature can be found on this subject and the mechanisms are still unclear. A certain combination of type and concentration of KHI and surfactant may possibly provide additional subcooling and hence reduce the dosage of THI´s in the drilling fluid in the future.

According to Kalogerakis et al. 1993 it was concluded through gas hydrate formation tests that the effects of different surfactants around their CMC´s did not affect the thermodynamics, but had a considerable effect on the kinetics. Hence, the use of some surfactants could change the rate of hydrate formation. Furthermore Ramaswamy et al. 2011 elucidate how hydrates may grow faster if the surfactant is present in a larger concentration than its CMC. This is explained by the process of micellization, which basically means when there are no surfaces or all the surfaces are covered micelles will start to form. This does not occur for all types of surfactants and different surfactants present different CMC´s. The surfactants will create diverse micelle structures based on molecular geometry and the properties of the fluid (concentration, salinity, temperature, pH etc.). Non-ionic surfactants have been shown to present micelles with several hundreds of molecules per micelle, while ionic ones have shown to present only up to a hundred due to electrostatic repulsions between head groups. The micelles will function as nucleation sites which in turn will increase gas hydrate formation. It is also illuminated that foaming (a property of many surfactants) may increase the gas-liquid interface area which consequently allows for faster nucleation and increased hydrate formation rates.

2.4 Hydrate testing

There are several macroscopic experimental methods for studying hydrate properties. Some of the equipment made for this purpose are autoclaves, rocking cells, high pressure rheometers, flow wheels and flow loops. The different equipment provides measurements like P_{diss} (hydrate dissociation pressures), T_{diss} (hydrate dissociation temperatures), gas consumption rates during growth/decomposition, visualization of growth/decomposition/agglomeration and measurements of viscosity/pressure changes. Test method is selected based on desired results as the methods have different capabilities and limitations (Sloan & Koh 2008).

In this study the Physica Rheometer – a high pressure rheometer was used (Figure 17).

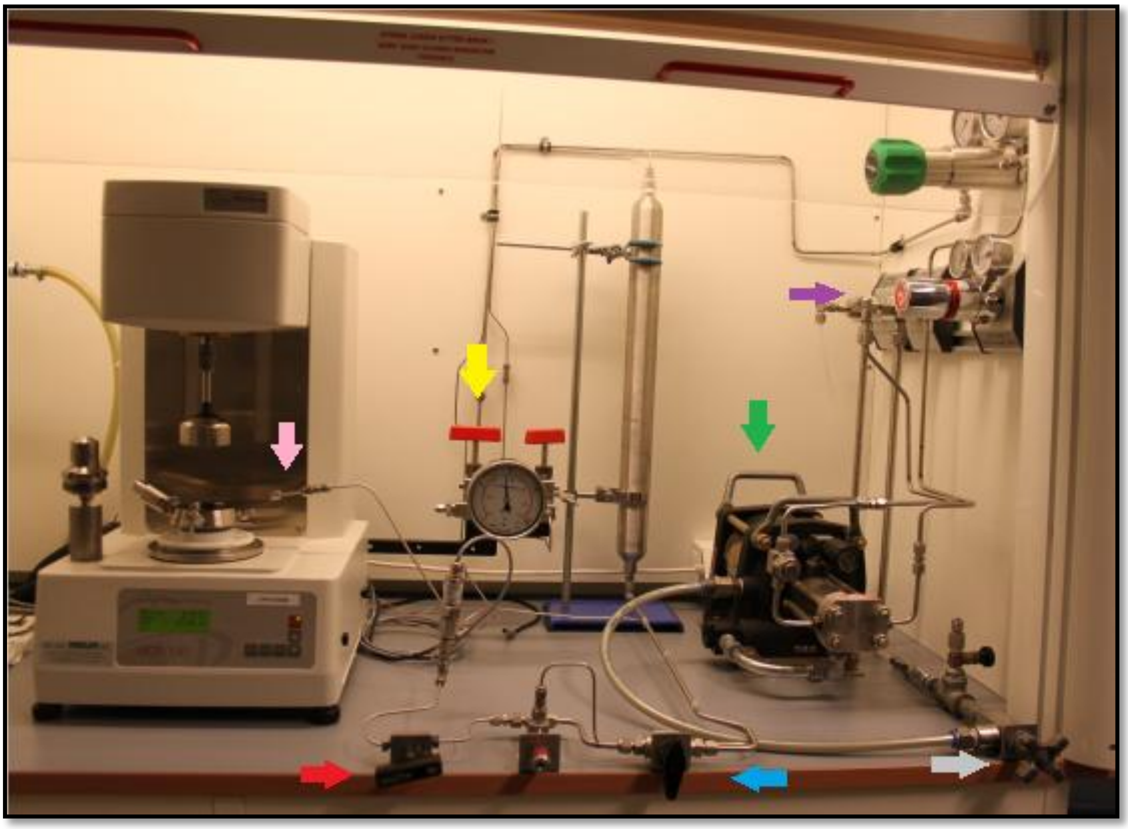


Figure 17: Physica Rheometer for gas hydrate testing (SWACO 2011a). The figure is edited.

This test equipment is developed by the R&D department at M-I SWACO together with gas hydrate research at the University of Stavanger (SWACO 2011a). The test equipment allows measurements of viscosity- and pressure changes versus time in drilling fluids. The drilling fluid is placed in a pressure cup, which is connected to a gas cylinder and a temperature- and a pressure sensor. A measuring cylinder with a pressure head seals the cell and is the rotating part. A magnetic coupling will give the pressure head and pressure cylinder torque.

Rheological properties can be measured at desired cooling rates provided by a cooling bath, and at desired pressures of natural gas or in a sealed environment. A computer will record and save the data. As gas hydrates starts to grow in the mud-cell due to the high pressure present and cooling, the recordings will provide a graph showing viscosity increase and pressure decrease at this point.

3 EXPERIMENTAL SETUP AND PROCEDURE

The purpose of this study was to evaluate different combinations of a kinetic gas hydrate inhibitor and various surfactants, used in a low density water-based mud system to study possible synergy effects of those combinations. Some combinations were thought to provide additional subcooling contribution than the KHI or the surfactants would provide alone.

Inhibitor performance was evaluated based on gas hydrate prevention capacity as the main focus, and in addition standard water-based drilling fluid properties was evaluated for compatibility. Evaluation of efficiency was thus done by standard water-based mud testing including rheology, pH-measurements and API filtration tests, and by constant-cooling rate tests on Physica Rheometer modified for gas hydrate formation testing.

A low inhibited base fluid and a KHI was chosen. Performance was tested on base fluid, on base fluid with KHI, on base fluid with different surfactants, and on base fluid with KHI together with different surfactants. In addition, performance was tested on base fluid with KHI together with two different anti-agglomerants based on particular results. Various concentrations of KHI and surfactant/anti-agglomerants and different classes of surfactants and special designed AA´s were used to evaluate performance and possible synergy effects. The order of addition of KHI and surfactant was also assessed.

3.1 Choosing, mixing and testing the base fluid

The purpose of this part of the experiment was to choose a base fluid that could be used for this study, mix it and investigate its properties.

Glydril, a well known low density WBM was chosen to be the base fluid in this study because of its frequent use in deepwater drilling in which it has shown good quality performance in the field. In addition the base fluid needed to be low inhibited (low concentrations of glycol and salt) to obtain hydrate formation at reasonable temperatures and pressures, and to distinguish the different inhibitors' performances more clearly.

The drilling fluid was mixed on a Silverson mixer (Figure 18) adjusted for WBM mixing. Products, properties, amounts and mixing times are shown in table 8.

Three standard M-I SWACO tests for WBM´s were performed on the low inhibited base fluid; pH-measurements, rheology and API fluid loss. The equipment used for these purposes was an Electronic glass-electrode pH-meter, a Fann 35 Viscometer (Figure 19) and an API Static Filter Press (Figure 20) respectively. Rheology and pH was measured before and after hot rolling (BHR and AHR) in an aging cell (Figure 21) and the rheology was performed at different temperatures. API was measured after hot rolling. After hot rolling, the drilling fluid was always mixed on a Hamilton Beach Mixer (Figure 22) to get the mud evenly mixed before doing any tests. The WBM tests on the base fluid were performed to evaluate if the later addition of KHI/surfactants/anti-agglomerants had changed any of these properties.

3.1.1 Equipment and products

Mixing of Glydril 1,1SG

- Mixing beaker (2,0 L)
- Scale
- Spoon
- Silverson mixer (L4/L4R/L5M)
- Spatula
- Syringes (20,0 mL)
- Bucket for cooling
- Timer
- Products (Table 8)

Figure 18: Silverson mixer (Ltd).

8: Glydril 1,1SG products, properties, amounts and mixing times.

Product	Properties	Amount (g/L)	Mixing time (min)
Freshwater	Base fluid	921,5	0
KCl	Density, shale inhibition, THI	50	2
Soda Ash	Adjust pH, Calcium precipitation, flocculation	1	2
Polypac ELV	Shale inhibition, reduce fluid loss, avoid uncontrollable viscosity build-up, lubricity, filtercake quality	15	10
DuoTec NS	Viscosity, highly shear-thinning and thixotropic properties	3	10
Glydril MC	Filtration control, wellbore stability, lubricity, reduce dilution rates and bit balling, THI	20	5
Barite (regular)	Density, weight material	89,5	30

pH-measurements

- Electronic glass-electrode pH-meter
- Buffer solutions (pH 4,0, 7,0 and 10,0)
- Deionized water

Rheology

- Fann 35 Viscometer
- Calibration equipment
- Sample of BHR and AHR Glydril 1,1SG
- Heating cup
- Thermometer
- Spatula
- Timer

Figure 19: Fann 35 Viscometer (SWACO 2011a).

API fluid loss

- Bottom part with outlet
- Wooden stand
- 2 sealing rings
- Sieve
- Special hardened filter paper for OFI low-pressure filter press (OFITE, diameter 3,5”)
- Body cell
- Sample of AHR Glydril 1,1SG
- Lid connected to a pressurized tube
- Measuring cylinder (10,0 mL)
- Timer

Figure 20: API Static Filter Press (SWACO 2011a).

Hot rolling and mixing on Hamilton Beach

- Aging cell
- Sample of Glydril 1,1SG (350 mL)
- Sealing ring
- Grease
- Lid with valve
- Lid
- Screwdriver
- Wrench
- HPHT-equipment for pressurizing the cell (High pressure)
- Mixing cup
- Spatula
- Hamilton Beach Mixer
- Timer
- Hot rolling oven

Pressurized Aging Cell (OFI Testing Equipment 2012).

Figure 21: Hamilton Beach Mixer with mixing cups (Fann 2012).

3.1.2 Procedures

1. Mix the drilling fluid according to standard M-I SWACO mixing procedures (APPENDIX A) for Glydril WBM on a Silverson mixer adjusted for WBM mixing.
2. Measure the pH according to standard M-I SWACO procedures (APPENDIX B) with a pH-meter on BHR sample.
3. Calibrate the Fann 35 viscometer according to standard M-I SWACO procedures (APPENDIX C).
4. Measure rheology of BHR sample at 50°C at speeds 600, 300, 200, 100, 6 and 3 rpm according to M-I SWACO procedures (APPENDIX D).
5. Hot roll 350mL of the sample according to standard M-I SWACO procedures (APPENDIX E) in an aging cell for 16 hours at 100°C. Pressurize the cell with 150psi to prevent boiling.
6. Transfer the sample to a mixing cup and mix on Hamilton Beach for 10 minutes to ensure an even mix.
7. Measure pH according to M-I SWACO procedures (APPENDIX B) and rheology of AHR sample at 2°C, 20°C and 50°C AHR according to M-I SWACO procedures (APPENDIX D). To get the right temperatures use a heating cup for the 50°C and 20°C measurements and a cup connected to a cooling bath for the 2°C measurement. Measure at speeds 600, 300, 200, 100, 6 and 3 rpm, in addition obtain 10 second and 10 minute gels.
8. Measure API fluid loss on AHR sample after 30 minutes at 100 psi according to standard M-I SWACO procedures (APPENDIX F).

3.2 Hydrate testing

The purpose of the experiment was to study the gas hydrate formation temperatures for Glydril 1,1SG base fluid, for Glydril 1,1SG base fluid with the selected KHI, for Glydril 1,1SG base fluid with various surfactants and for Glydril 1,1SG base fluid with the selected KHI and various surfactants, to evaluate the hydrate inhibition performance of the different additives and combinations. Some of these combinations were thought to present synergy effects that would provide additional subcooling than any of these additives would provide alone. The different combinations were thought to present different synergy effects due to concentration and surfactant type, and hence give varied performance. Performance was also evaluated for Glydril 1,1SG with KHI and two types of anti-agglomerants based on particular test results with the surfactants. The order of addition of KHI and surfactant was also assessed, as this presents different chemical reactions and hence a difference in performance.

The base fluid was mixed with KHI and surfactants/anti-agglomerants for 10 minutes each, on a Hamilton Beach mixer. Gas hydrate formation temperatures was employed by performing constant cooling rate tests on these samples using Physica Rheometer modified for gas hydrate formation testing (Figure 17).

The chosen KHI for this study was Luvicap 55w. The reason for this choice was that Luvicap 55w is a commercially available kinetic inhibitor which has shown good results in the field. A maximum concentration of 12000ppm (12 g/L) Luvicap 55w (50% active) was set for this study as typical dosages of KHI are 0,2-1,0 wt.% of active substance based on the water present in the drilling fluid.

The surfactants and anti-agglomerants were selected in collaboration with the R&D/PT department at M-I SWACO. A cationic, an anionic, an amine-oxide and a non-ionic surfactant were evaluated to cover most of the main classes of surfactants. These classes have different surface properties, and thus different synergy effects were thought to be achieved with the KHI. The surfactants were chosen based on their chain lengths (about 12C) which are typical for anti-agglomerants. The surfactants also had to be water soluble and highly surface active (in which 12C surfactants are). In addition these surfactants are commercially available in large scale. The two anti-agglomerants selected was designed by M-I SWACO and their structures are confidential due to a commercial perspective. These compounds have typical anti-agglomerant structures with some enhancements; they are quaternary ammonium compounds mainly used as traditional anti-agglomerants and have proven good results for this purpose. In this study the AA´s was rather employed due to their surfactant behavior.

In addition, standard WBM tests (as described in chapter 3.1) were performed on Glydril 1,1SG with some of the various combinations of KHI and surfactants to evaluate if the mud properties had changed due to these additions. Changes in mud properties were evaluated together with the hydrate formation temperatures to achieve a functional combination that could be used in the field.

3.2.1 Equipment

Mixing of Glydril 1,1SG with KHI and/or surfactants/anti-agglomerants

- A 250 mL (275,0 g) sample of BHR Glydril 1,1SG
- Mixing cup
- Scale
- Desired concentrations of KHI and surfactants/anti-agglomerants
- Pipette
- Hamilton Beach mixer
- Timer
- Defoamer (EMI 1705)

Gas hydrate tests with Physica Rheometer

- Physica Rheometer with associated parts
- A 10,0 mL sample of Glydril 1,1SG mixed with selected KHI and/or surfactants/anti-agglomerants
- Syringe (12,0 mL)
- Cloths
- Wash bottle with deionized water
- Special wrench for pressure cell
- Adjustable wrench
- Pliers for snap ring
- Small special screwdriver
- Q-tips
- Snoop Liquid Leak Detector

The Physica Rheometer associated parts are shown in figure 23 and 24.

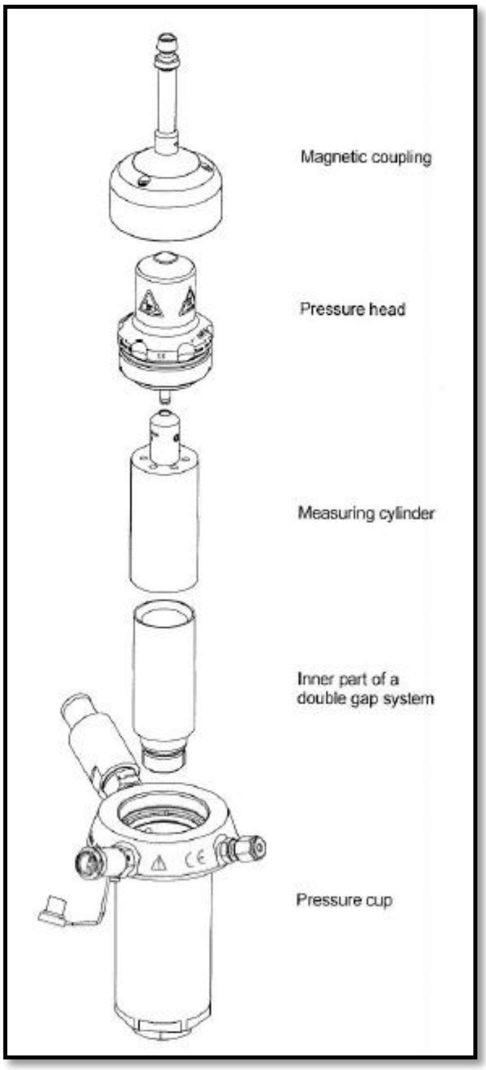


Figure 22: Overview and assembly of pressure cell parts (Paar 2007).

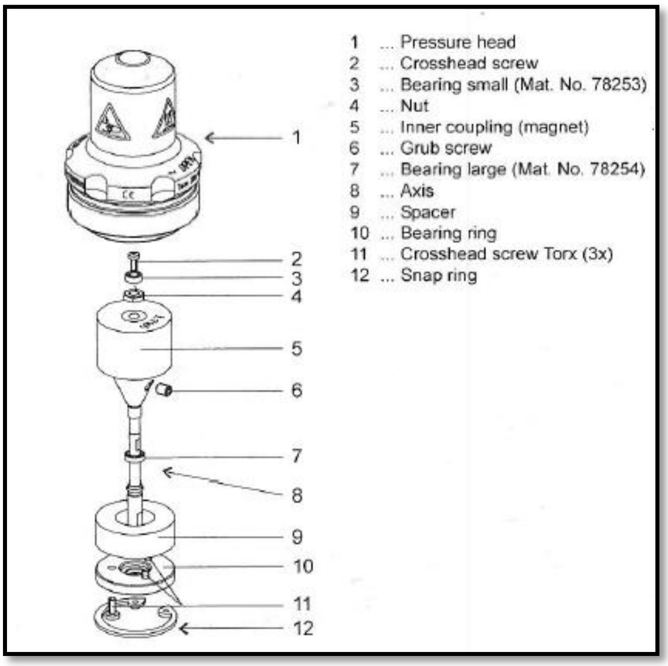


Figure 23: Overview and assembly of pressure head parts (Paar 2007).

Other associated parts include:

- O-ring
- Pressure and temperature sensors
- Pressure supply of natural gas
- Gas cylinder
- Booster
- Cooling bath supplying cooling to the system
- Valves (open/close/safety)
- Connectors, cables and tubes

(Detailed information about the different parts can be found the instruction manual (Paar, 2007))

Figure 25 shows an assembled pressure cell ready for use.

Figure 24: An assembled pressure cell (Paar).

3.2.2 Chemicals and gas mixture

Table 9 shows the types, names, classes and activities of additives used in this study. The table also show information about barite, Polypac ELV and Duotec NS which are some of the components in Glydril 1,1SG assumed to affect mechanisms in this study. Structures can be found in APPENDIX G. Safety datasheets for all chemicals used in this study can be found in APPENDIX H. Table 10 shows the natural gas mixture (Green Canyon) supply to the Physica Rheometer.

Table 9: Overview of additives used in this study.

Product type	Product name	Chemical name	Class	Ionic type/Surface charge	Estimated Activity
KHI	Luvicap 55W	Vinylcaprolactam/Vinylpyrrolidone copolymer (1:1)	Polymer		50%(l)
Defoamer	EMI-1705		Light-hydrotreated petroleum distillate		60-100%(l)
Surfactant	Arquad 12-30	Dodecyltrimethyl ammoniumchloride	Quaternary ammonium	Cationic	40% (l)
Surfactant	SDS	Sodium dodecyl sulphate	Sulphate	Anionic	100% (s)
Surfactant	Aromox C/12-W	Bis(2-Hydroxyethyl) Cocoamine Oxide	Alkylethylamine oxide	Non-ionic in neutral and alkaline environments	40% (l)
Surfactant	Imbentin-AG/124S/040	Alcohol C12-14 + 4 EO	Fatty alcohol ethoxylate	Non-ionic	50% (l)
Anti-agglomerant	Cdld-151	*Confidential General name: (Tri-n-butyl)-n-tetradecylphosphonium chloride	Quaternary ammonium	Cationic	50%(l)
Anti-agglomerant	Cdld-445	*Confidential General name: (Tri-n-butyl)-n-tetradecylphosphonium chloride	Quaternary ammonium	Cationic	50%(l)
Drilling fluid weight material	Barite (regular)	Bariumsulphate	Sulphate	Anionic	100%(s)
Drilling fluid fluid loss additive	Polypac ELV	Main component: Carboxymethyl cellulose	Cellulose derivative	Anionic	100%(s)
Drilling fluid viscosifier	Duotec NS	Main component: Xanthan Gum	Polysaccharide	Anionic	100%(s)

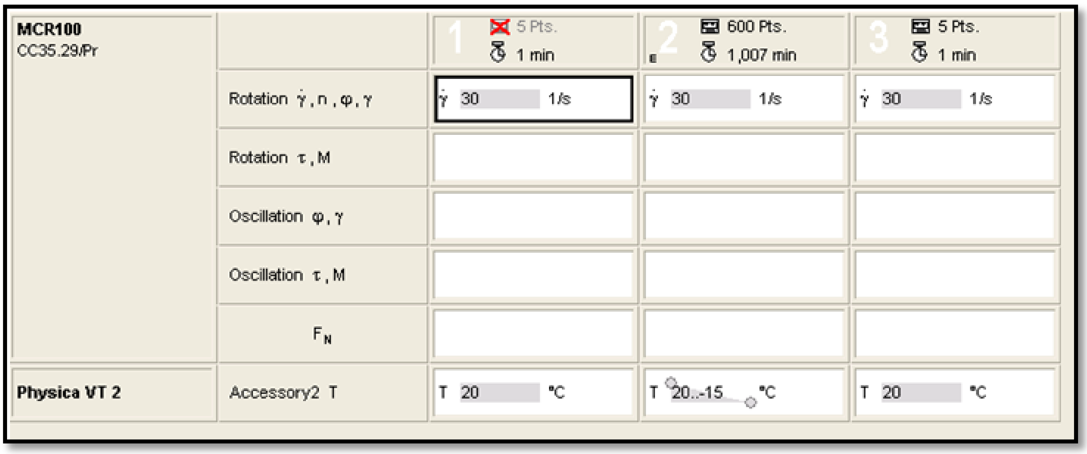
* AA´s developed by M-I PT.

Table 10: Gas mixture (Green Canyon) components and concentrations.

Component	Nominal Concentration
Pentane n-	0,200 %
Pentane iso	0,200 %
Butane iso	0,500 %
Propane	3,100 %
Butane n-	0,800 %
Nitrogen	0,400 %
Ethane	7,600 %
Methane	87,20 %

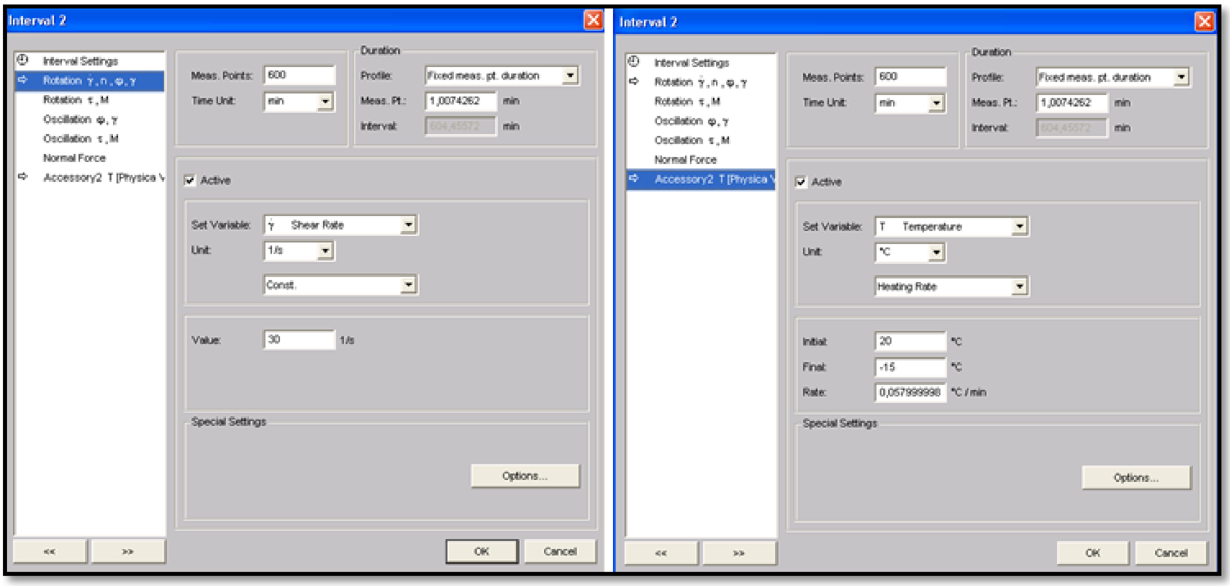
3.2.3 Put on a constant cooling rate test (Physica Rheometer)

1. The Rheometer software Rheoplus´ settings used in this experiment are shown in figure 26. These settings are standard for this type of test. Rotation is set to 30 1/s for all three intervals. The first interval is a 5 minute interval, without measuring points, to stabilize the sample at 20°C before start. The second interval´s measurements will be obtained every 1,007 minute, and a total of 600 measuring points at a cooling rate of 0,058°C per min (settings for interval 2 shown in figure 27). If the torque value exceeds 99000 µNm (settings shown in figure 28) the test will shift to interval 3 before the 600 points are measured, as the hydrate growth is sufficient and to avoid excessive wear out of the equipment. In interval 3, the sample is heated for 5 minutes and the temperature is set to 20°C without measuring points.



MCR100 CC35.29/Pr		1 5 Pts. 1 min	2 600 Pts. 1,007 min	3 5 Pts. 1 min
	Rotation $\dot{\gamma}, n, \varphi, \gamma$	$\dot{\gamma}$ 30 1/s	$\dot{\gamma}$ 30 1/s	$\dot{\gamma}$ 30 1/s
	Rotation τ, M			
	Oscillation φ, γ			
	Oscillation τ, M			
	F_N			
Physica VT 2	Accessory2 T	T 20 °C	T 20...-15 °C	T 20 °C

Figure 25: Rheoplus settings.



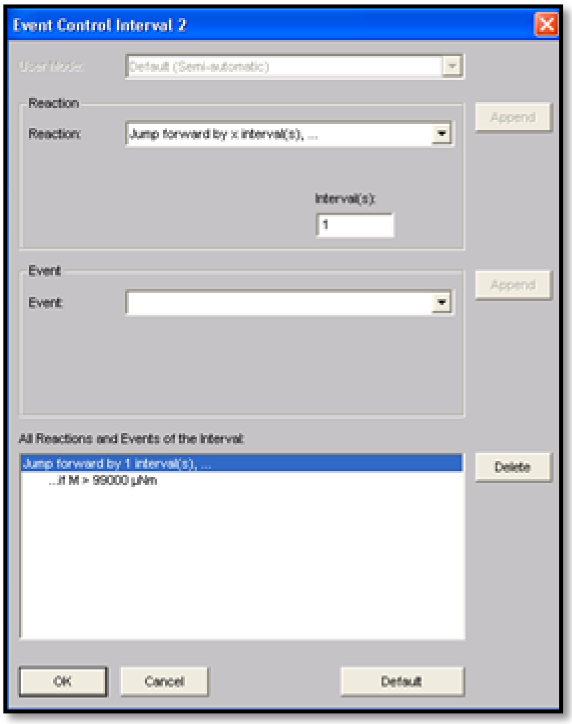
Interval 2

Meas. Points: 600
Time Unit: min
Duration
Profile: Fixed meas. pt. duration
Meas. Pt.: 1,0074262 min
Interval: 604,45572 min
☑ Active
Set Variable: γ̇ Shear Rate
Unit: 1/s
Const.
Value: 30 1/s

Interval 2

Meas. Points: 600
Time Unit: min
Duration
Profile: Fixed meas. pt. duration
Meas. Pt.: 1,0074262 min
Interval: 604,45572 min
☑ Active
Set Variable: T Temperature
Unit: °C
Heating Rate
Initial: 20 °C
Final: -15 °C
Rate: 0,057999998 °C / min

Figure 26: Settings for interval 2.



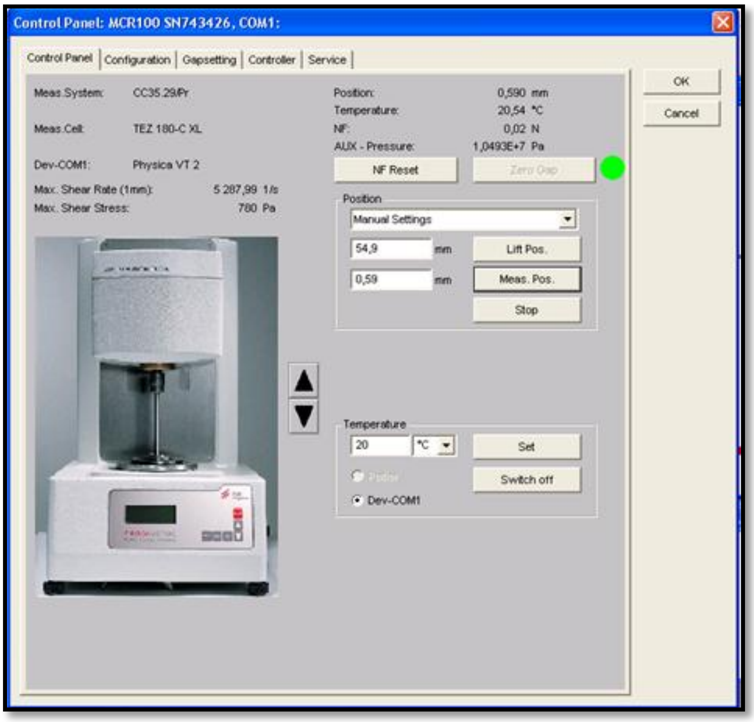
Event Control Interval 2

User Mode: Default (Semi-automatic)
Reaction
Reaction: Jump forward by x interval(s), ...
Interval(s): 1
Event
Event:
All Reactions and Events of the Interval:
Jump forward by 1 interval(s), ...
...if M > 99000 µNm

Figure 27: Settings for maximum torque.

2. The parts in point 2-11 in figure 24 are an assembly that is only disassembled if some of the parts need to be replaced. Make sure the equipment is clean, that bearings rotate smoothly and evenly, and that the bearings are free from rust.
3. This assembly is put into the pressure head (part 1, figure 24) and is fixed with a snap ring (part 12, figure 24) with pliers. Make sure the snap ring is free from rust.

4. Connect the measuring cylinder to this assembly using a special screwdriver. Make sure that the screw is fixed into the notch and is pressed as far in to the pressure head as possible. The whole assembly is shown in figure 23.
5. Put a 10,0 mL sample of mud in the pressure cup using a syringe. Make sure that there are no air bubbles in the mud, and that the mud is about 20°C. If the mud is freshly mixed it may be hot and thus need some cooling in room temperature. Leave the syringe for some minutes to cool. If the mud holds a lot of foam/air bubbles, leaving it in the mixing cup for a while or using defoamer may help.
6. Put the o-ring into the pressure cup. Make sure that it fits properly, if the O-ring is just used in a previous test it may have gotten enlarged due to the pressure applied. Make sure that the o-ring is smooth and not damaged.
7. Put this whole assembly gently down into the pressure cup and turn the pressure head until it’s fastened. Reinforce with the help of a special wrench for the pressure cell.
8. Connect the gas supply tube to the pressure cup (pink arrow, figure 17). Use an adjustable wrench to fasten the screw nut.
9. Turn on the gas supply from the cylinder turning the black switch (blue arrow, figure 17) to the left. Then let this gas into the cell using the blue safety switch (red arrow, figure 17) by turning this to the left. The cylinder pressure will be somewhat decreased and a sound of the pressure going into the cell will be noticed.
10. Flush the cell by closing the black switch and by opening the screw nut with the adjustable wrench to let the gas out of the cell. Fasten the screw nut and open the black switch to fill the cell again. This is done three times. Test for leakage around the screw nut by using Snoop which is shaken to create foam, and then squeezed onto this area.
11. Fill the cell again by turning the black switch, and then close it.
12. Turn on the natural gas supply and the compressed-air (purple arrow, figure 17) supply for the booster (green arrow, figure 17). Turn on the booster by turning the grey switch (grey arrow, figure 17) to the left.
13. When the booster pressure is about 100 bar, open up to the cylinder by turning the red switch (yellow arrow, figure 17) to the left.
14. Open the black switch to pressurize the cell. Test again for leakage using Snoop.
15. Press the button that looks like a rheometer on the Rheoplus program; this will show the control panel (figure 29). Wait until the pressure in the cell shows about 105-107 bar (to ensure approximately 100 bars when hydrates are formed). When sufficient pressure is achieved, close the black switch.
16. Keep filling the cylinder until it shows about 110 bar. Then close the grey switch, the red switch and then the natural gas- and compressed air supply switches. Close the blue switch.
17. Attach the magnetic coupling and put it in the measuring position (the magnetic coupling will be lowered) in the control panel. Select a value (mm) for the measuring position that ensures the NF value (N) to be slightly above zero (about 0,05N).


Control Panel: MCR100 SN743426, COM1:

Meas.System: CC35.29/Pr
Meas.Cell: TEZ 180-C XL
Dev-COM1: Physica VT 2
Max. Shear Rate (1mm): 5 287,99 1/s
Max. Shear Stress: 780 Pa

Position: 0,590 mm
Temperature: 20,54 °C
NF: 0,02 N
AUX - Pressure: 1,0493E+7 Pa

Position: Manual Settings
54,9 mm
0,59 mm

Temperature: 20 °C
● Dev-COM1

Figure 28: Control panel settings.

18. Press ok, and then press the play button in the main display to start the test. Check if the pressure is constant during the first five minutes to ensure that there are no leakages.
19. Wait about 10h until the test is finished and has stopped. The test may stop earlier than this (an earlier shift to interval 3) if the torque is too high.
20. Graphs showing the pressure/temperature/viscosity relationship versus time for the measured sample will be displayed. Hydrate formation is shown by a sudden decrease in pressure and a sudden increase in viscosity.

3.2.4 Take off a test (Physica Rheometer)

1. Open the control panel and set the magnetic coupling to the lift position (the magnetic coupling will be lifted). Detach the magnetic coupling.
2. Use the adjustable wrench to release the pressure from the cell by loosening the screw nut. Be careful and use an oil cloth as mud may spatter vigorously from the opening. Wash the pressure supply tube with a wash bottle.
3. Use the special wrench to loosen the pressure head.
4. Remove the mud from the pressure cup by using a syringe and clean the cell with deionized water using a wash bottle. Use a cloth to dry the cell.
5. Disassemble the pressure cell parts and rinse carefully with water. Make sure that all equipment is dry and rust free. Use a Q-tip for small openings and use compressed air to dry properly.

3.2.5 Reading the results (Physica Rheometer)

Figure 30 shows an example of a graph obtained from a constant cooling rate test. Hydrate formation can be seen in this graph as a sudden vertical decrease in pressure (green curve) and by a sudden vertical increase in viscosity (blue curve). The temperature (red graph) decreases due to the cooling rate, and increases after a peak of hydrates as the torque has exceeded the selected limit value and the test moves to the warm-up interval. The hydrate formation temperature is found by reading the temperature graph at the point where the viscosity has a sudden increase. In addition, a sudden decrease in pressure will also be an indication and can be employed to double-check the result. Rheoplus also provide a list (figure 31) of the different values (time, temperature, viscosity, pressure etc.) in addition to the graph. The right results will be obtained by checking this list for temperatures where an increase in viscosity and a decrease in pressure is present.

The additional subcooling provided by a certain combination obtained from these test results was calculated as follows:

"The average hydrate formation value for the base fluid minus the average hydrate formation temperature of the samples."

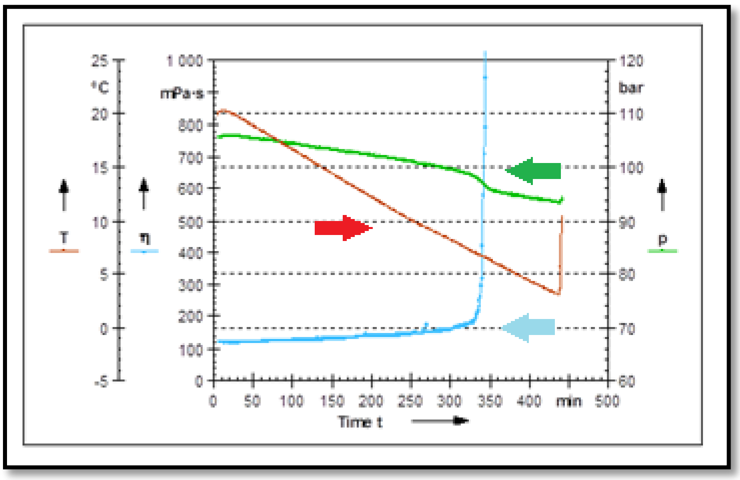
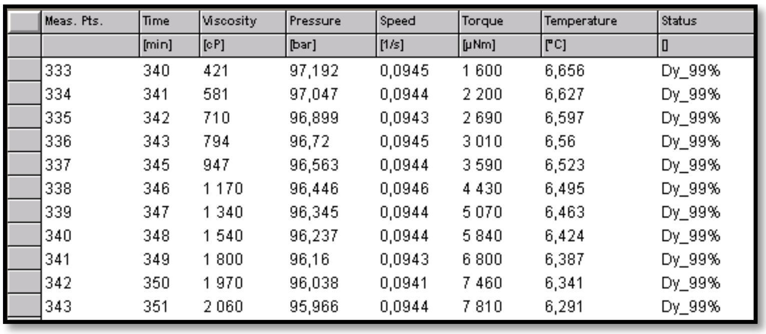


Figure 29: Example of a graph obtained from a constant cooling rate test. The red arrow points at the constant temperature decrease graph, the blue arrow points at the point where the viscosity graph shows a sudden increase in viscosity and hence catastrophic hydrate growth, and the green arrow points at the point where the pressure graph shows a sudden decrease in pressure.



Meas. Pts.	Time	Viscosity	Pressure	Speed	Torque	Temperature	Status
	[min]	[cP]	[bar]	[1/s]	[µNm]	[°C]	[]
333	340	421	97,192	0,0945	1 600	6,656	Dy_99%
334	341	581	97,047	0,0944	2 200	6,627	Dy_99%
335	342	710	96,899	0,0943	2 690	6,597	Dy_99%
336	343	794	96,72	0,0945	3 010	6,56	Dy_99%
337	345	947	96,563	0,0944	3 590	6,523	Dy_99%
338	346	1 170	96,446	0,0946	4 430	6,495	Dy_99%
339	347	1 340	96,345	0,0944	5 070	6,463	Dy_99%
340	348	1 540	96,237	0,0944	5 840	6,424	Dy_99%
341	349	1 800	96,16	0,0943	6 800	6,387	Dy_99%
342	350	1 970	96,038	0,0941	7 460	6,341	Dy_99%
343	351	2 060	95,966	0,0944	7 810	6,291	Dy_99%

Figure 30: A list of values is presented to check the results. From measuring point 333 the viscosity and torque starts to increase rapidly, hence the hydrate formation temperature is 6,6^{o}C.

3.2.6 Testing the base fluid – Constant cooling rate tests

A 10,0 mL sample of freshly mixed Glydril 1,1SG was put into the pressure cup for gas hydrate formation temperature measurements. The test was performed according to the steps in subchapter 3.2.3 and 3.2.4. Repeats were performed to confirm the test results. These test results was used for the comparison with the addition of KHI and/or surfactants and for the addition of KHI and anti-agglomerants, to see if hydrates could be formed at lower temperatures as a result of subcooling contribution from these additives.

3.2.7 Testing the base fluid with KHI – Constant cooling rate tests

Freshly mixed Glydril 1,1SG was mixed with two different concentrations of Luvicap 55w on Hamilton Beach for 10 minutes. Samples of 10,0mL were put into the pressure cup for gas hydrate formation temperature measurements. The test was performed according to the steps in subchapter 3.2.3 and 3.2.4. Table 11 shows the different concentrations and amounts measured. The two different concentrations were measured to see if a higher concentration would give better performance (lower the hydration formation temperature). Repeats were performed to confirm the test results.

A concentration of 12000ppm was decided at a project meeting, to be the maximum value of KHI/surfactants/anti-agglomerants as this is a common dosage of KHI. The concentration of 12000ppm Luvicap 55w was also decided to be tested to obtain an end-point on the KHI side, which could show the effect of maximal dosage of only Luvicap 55w. The purpose of this was to lower the concentration of Luvicap 55w and thus increase the dosage of surfactants/anti-agglomerants to see if this could contribute to a higher degree of subcooling than the Luvicap 55w would do alone. It was thought that different synergy effects would appear from different concentration variations and different types of additives.

Table 11: Concentrations and amounts of Luvicap 55w tested.

Additive and concentration	Components	Amounts
Luvicap 55w (6000ppm)	Glydril 1,1SG Luvicap 55w	275,0 g 1,5 g
Luvicap 55w (12000ppm)	Glydril 1,1SG Luvicap 55w	275,0 g 3,0 g

3.2.8 Testing the base fluid with various surfactants – Constant cooling rate tests

Freshly mixed Glydril 1,1SG was mixed with various surfactants on Hamilton Beach for 10 minutes. Samples of 10,0mL were put into the pressure cup for gas hydrate formation temperature measurements. The test was performed according to the steps in subchapter 3.2.3 and 3.2.4. Table 12 shows the different types of surfactants, concentrations and amounts tested. Repeats were performed to confirm the test results. Activities were taken into account to obtain the same activities as for Luvicap 55w (50%).

The tests were performed on both 6000ppm and 12000ppm of surfactant to study if a higher concentration would affect the hydration formation temperature. As for the Luvicap 55w, the tests on 12000ppm were performed to obtain an end-point on the surfactant side, to show the effect of maximal dosage of only surfactant. The purpose of this was to lower the concentration of surfactant and thus increase the dosage of Luvicap 55w to see if this could contribute to a higher degree of subcooling than the surfactants would provide alone. It was thought that different synergy effects would appear from different concentration variations and types of additives. Constant cooling rate tests of base fluid with the addition of the two anti-agglomerants were not performed due to time constraints.

Table 12: Concentrations and amounts of surfactants tested.

Additive and concentration	Components	Amounts
Arquad 12-30 (6000ppm)	Glydril 1,1SG Arquad 12-30	275,0 g 1,5 g
Arquad 12-30 (12000ppm)	Glydril 1,1SG Arquad 12-30	275,0 g 3,0 g
Aromox C/12-W (12000ppm)	Glydril 1,1SG Aromox C/12-W	275,0 g 3,0 g
SDS (12000ppm)	Glydril 1,1SG SDS	275,0 g 7,5 g
SDS (6000ppm)	Glydril 1,1SG SDS	275,0 g 3,75 g
Imbentin-AG/124S/040 (12000ppm)	Glydril 1,1SG Imbentin-AG/124S/040	275,0 g 3,0 g
Imbentin-AG/124S/040 (6000ppm)	Glydril 1,1SG Imbentin-AG/124S/040	275,0 g 1,5 g

* The SDS product was a solid (100% activity). This powder was diluted 1/5 with water (20% active) and added as a solution.

3.2.9 Testing the base fluid with KHI in combination with various surfactants/anti-agglomerants – Constant cooling rate tests

Freshly mixed Glydril 1,1SG was mixed with KHI and various surfactants/anti-agglomerants on Hamilton Beach – each component for 10 minutes. The surfactant/anti-agglomerant was always added prior to the KHI. Samples of 10,0mL were put into the pressure cup for gas hydrate formation temperature measurements. The test was performed according to the steps in subchapter 3.2.3 and 3.2.4. Table 13 shows the concentrations and amounts of surfactants/anti-agglomerants together with KHI measured. Repeats were performed to confirm the test results. Activities were taken into account to obtain the same activities as for Luvicap 55w (50%).

Maximum concentration of KHI and surfactant/anti-agglomerant was set to be 12000ppm in total as this was the standard concentration of KHI. Initially, a combination of 6000ppm/6000ppm of KHI and surfactant/anti-agglomerant was decided to be added. By doing this, eventual synergy and antagony effects would appear as these test results were compared to the test results of base fluid with only Luvicap 55w or surfactants/anti-agglomerants. It was thought that the right combination of KHI and surfactant/anti-agglomerant type would lower the hydrate formation temperature more than any of these additives would accomplish alone due to their different surface properties.

For the combination which showed the most promising results and where synergy effects were clearly present at this ratio, further tests with other concentration variations was performed. These concentration variations were performed to see how these synergy effects would be affected by the varying ratios in order to lower the hydrate formation temperature even more. The right concentration combination was thought to contribute to even further subcooling as a result of maximum synergy effects between the KHI and surfactant. The concentration ratios chosen for this purpose was thus 9000ppm/3000ppm of KHI and surfactant and the opposite, and 7000ppm/5000ppm of KHI and surfactant and the opposite.

Only one parallel of KHI with each of the two anti-agglomerants was performed due to time constraints. The KHI and anti-agglomerants were added in the ratio 6000ppm/6000ppm. The anti-agglomerant was tested as it was considered an analogue to the surfactant with the most promising results.

At a point, the order of addition was switched from adding the surfactant first and then the KHI to the other way around to assess the effect of the reverse order. This was done for the 6000ppm Luvicap 55w/6000ppm Arquad 12-30 sample. The test was performed to confirm the theory of that by adding the surfactant prior to the KHI, this would achieve enhanced performance. This was discussed in a meeting with chemists at M-I SWACO before the project started. It was thought that this would enhance surfactant adsorption on particles in the drilling fluid and hence improve the KHI performance.

Table 13: Concentrations and amounts of of Luvicap 55w and surfactants/anti-agglomerants tested.

Additives and concentrations	Components	Amounts
Arquad 12-30 (6000ppm) Luvicap 55w (6000ppm)	Glydril 1,1SG Arquad 12-30 Luvicap 55w	275,0 g 1,5 g 1,5 g
Arquad 12-30 (3000ppm) Luvicap 55w (9000ppm)	Glydril 1,1SG Arquad 12-30 Luvicap 55w	275,0 g 0,75 g 2,25 g
Arquad 12-30 (9000ppm) Luvicap 55w (3000ppm)	Glydril 1,1SG Arquad 12-30 Luvicap 55w	275,0 g 2,25 g 0,75 g
Arquad 12-30 (5000ppm) Luvicap 55w (7000ppm)	Glydril 1,1SG Arquad 12-30 Luvicap 55w	275,0 g 1,25 g 1,75 g
Arquad 12-30 (7000ppm) Luvicap 55w (5000ppm)	Glydril 1,1SG Arquad 12-30 Luvicap 55w	275,0 g 1,75 g 1,25 g
Aromox C/12-W (6000ppm) Luvicap 55w (6000ppm)	Glydril 1,1SG Aromox C/12-W Luvicap 55w	275,0 g 1,5 g 1,5 g
SDS (6000ppm) Luvicap 55w (6000ppm)	Glydril 1,1SG SDS Luvicap 55w	275,0 g 3,75 g 1,5 g
Imbentin-AG/124S/040 (6000ppm) Luvicap 55w (6000ppm)	Glydril 1,1SG Imbentin-AG/124S/040 Luvicap 55w	275,0 g 1,5 g 1,5 g
Cldl-151 (6000ppm) Luvicap 55w (6000ppm)	Glydril 1,1SG Cdld-151 Luvicap 55w	275,0 g 1,5 g 1,5 g
Cldl-445 (6000ppm) Luvicap 55w (6000ppm)	Glydril 1,1SG Cdld-445 Luvicap 55w	275,0 g 1,5 g 1,5 g

* The SDS product was a solid (100% activity). This powder was diluted 1/5 with water (20% active) and added as a solution.

3.3 Compatibility testing

As the KHI and surfactants/anti-agglomerants may alter the properties of the drilling fluid, standard WBM tests were performed with the addition of these, according to the procedures in subchapter 3.1.2 (step 2-8). The different surfactants/anti-agglomerants and KHI were mixed into the freshly mixed Glydril 1,1SG on the Silverson mixer, each component for 10 minutes. The surfactants/anti-agglomerants was added prior to the KHI. Table 14 shows the different KHI and surfactants/anti-agglomerants and concentrations on which standard WBM testing for compatibility was performed. Tests were not performed on Aromox C/12-W + Luvicap 55w due to the foaming and hence the obvious poor mud quality.

Table 14: Overview of additives and concentrations for standard WBM compatibility testing.

Additives	Concentration
Luvicap 55w	12000ppm
Luvicap 55w + Arquad 12-30	6000ppm + 6000ppm
Luvicap 55w + SDS	6000ppm + 6000ppm
Luvicap 55w + Aromox C/12-W	X
Luvicap 55w + Imbentin-AG/124S/040	6000ppm + 6000ppm
Luvicap 55w + Cdld-151	6000ppm + 6000ppm
Luvicap 55w + Cdld-445	6000ppm + 6000ppm

4 RESULTS

4.1 Standard WBM tests on base fluid

The selected standard WBM tests on Glydril 1,1SG base fluid was only performed for the comparison with the addition of the KHI/surfactants/anti-agglomerants, to make sure these additives did not affect the fluids performance. Results are shown in APPENDIX I.

4.2 Base fluid – Constant cooling rate tests

When performing the constant cooling rate tests on the Physica Rheometer many tests failed due to equipment failure or due to rusty or worn out ball bearings. This required replacement of parts, a warm-up sequence and calibration with both air and calibration fluid. One day was lost every time this happened. The equipment is supposed to be rust-free according to the producer, which is not the case when using natural gas (Green Canyon).

Figures 32 and 33 show two parallel results (1G and 2G) of constant cooling rate tests on Glydril 1,1SG base fluid. Figures 30 and 31 show hydrate formation in the base fluid at 6,7^{o}C and 7,6^{o}C respectively at about 100 bar. The average formation temperature was thus 7,2^{o}C. An overview of results is shown in table 15.

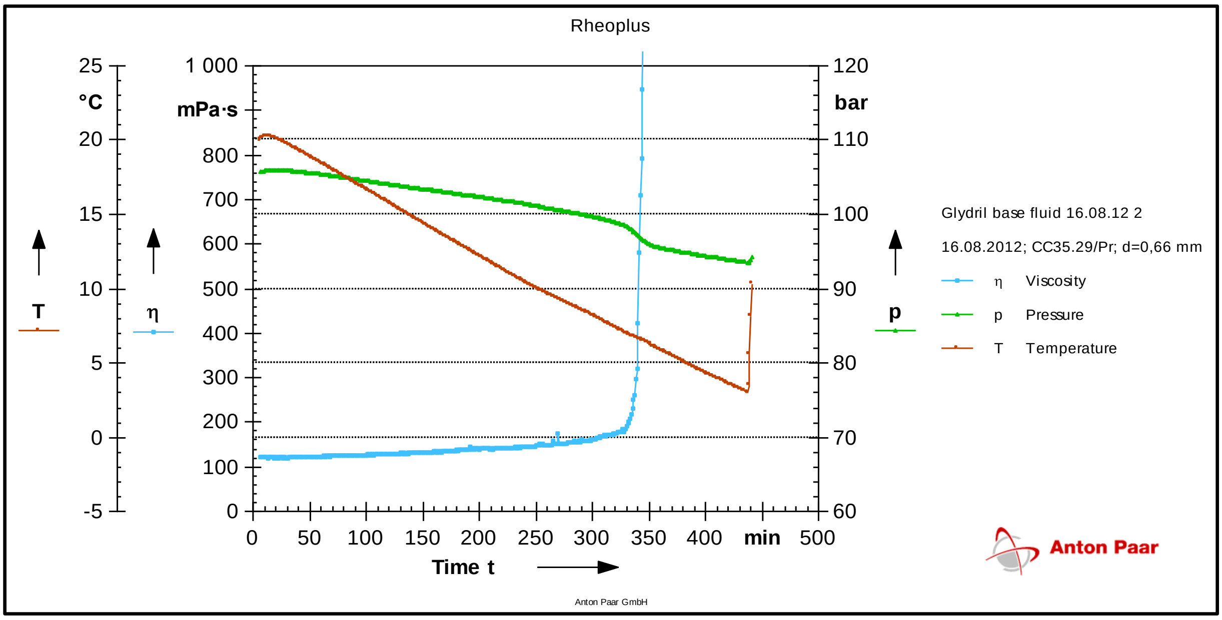


Figure 31: Parallel 1G - Constant cooling rate test on Glydril 1,1SG base fluid. The graph shows hydrate formation at 6,7^{o}C.

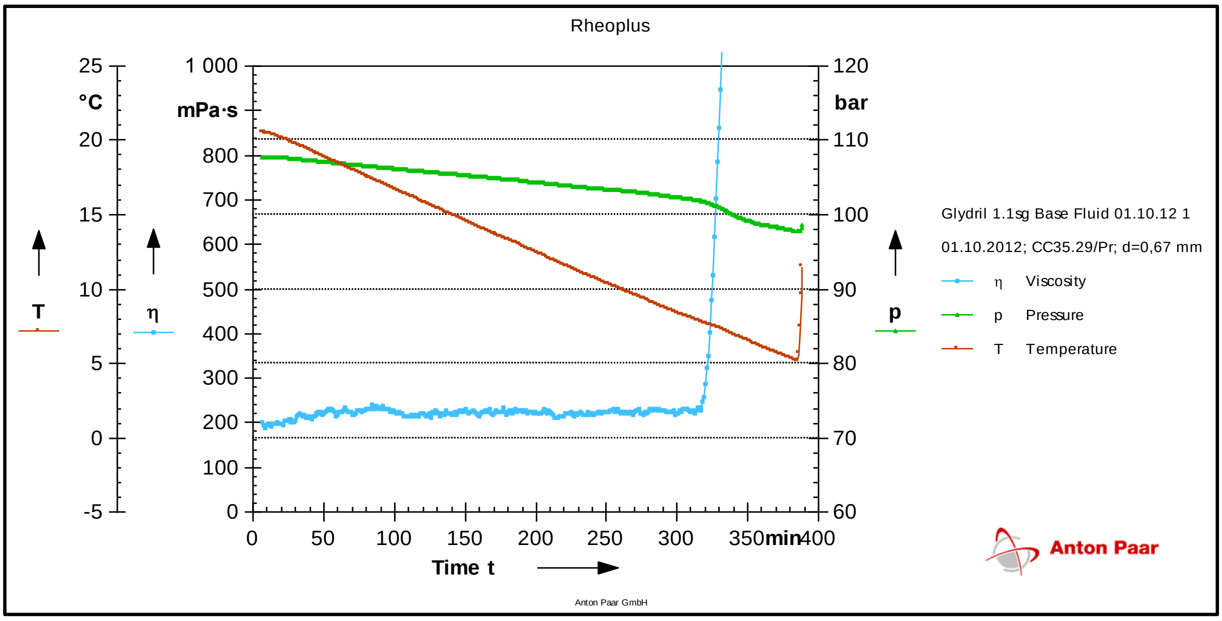


Figure 32: Parallel 2G - Constant cooling rate test on Glydril 1,1SG base fluid. The graph shows hydrate formation at 7,6°C.

Table 15: Overview of results of constant cooling rate tests on Glydril 1,1SG base fluid.

Test date	Description	Parallel	Hydrate formation temperature (°C)	Average (°C)
16.08.2012	Glydril 1.1SG base fluid	1G	6,7	
01.10.2012	Glydril 1.1SG base fluid	2G	7,6	7,2

4.3 Base fluid with KHI – Constant cooling rate tests

Figures 34 and 35 show four parallel results ($1L_{6000}$, $2L_{6000}$, $3L_{6000}$ and $4L_{6000}$) of constant cooling rate tests on Glydril 1,1SG base fluid with the addition of 6000ppm Luvicap 55w. The figures show hydrate formation at 2,0°C, 3,3°C, 1,7°C and 3,0°C respectively at about 100 bar. The average temperature was thus 2,5°C. Figure 36 shows two parallel results ($1L_{12000}$ and $2L_{12000}$) of constant cooling rate tests on Glydril 1,1SG base fluid with the addition of 12000ppm Luvicap 55w. The figure shows hydrate formation at 1,8°C and 1,8°C respectively at about 100bar. The average temperature was thus 1,8°C. An overview of results is shown in table 16.

Luvicap 55w is almost odorless and is not irritating.

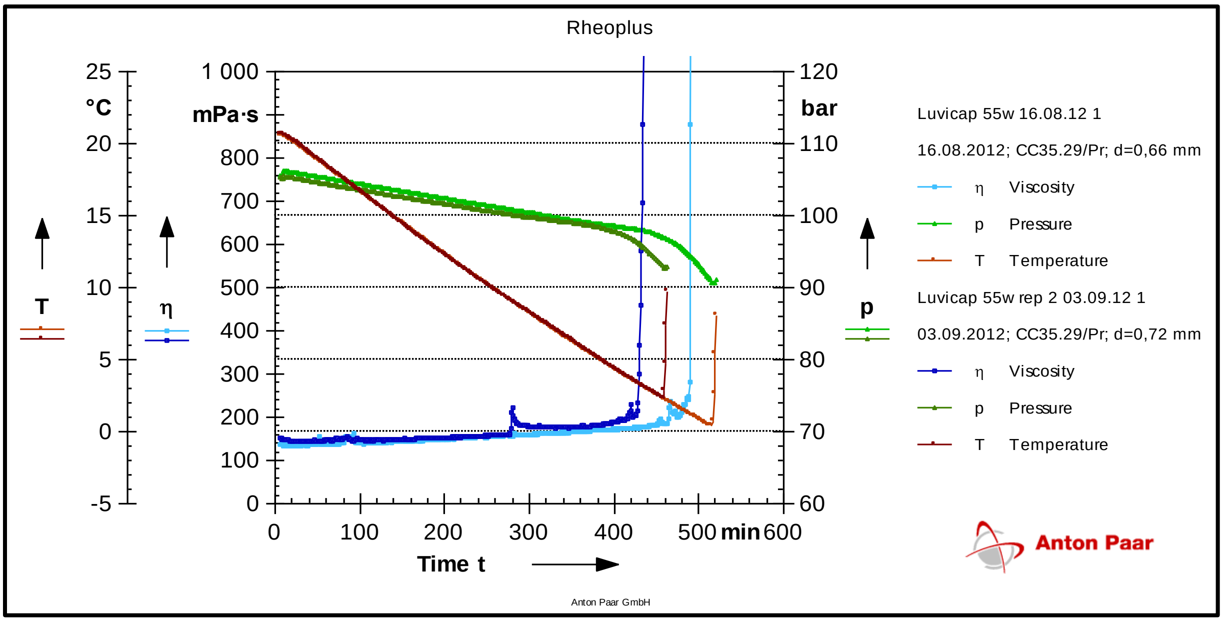


Figure 33: Parallel $1L_{6000}$ (light blue) and $2L_{6000}$ (dark blue) – Constant cooling rate tests on Glydril 1,1SG base fluid with 6000ppm of Luvicap 55w. The graphs show hydrate formation at 2,0°C and 3,3°C respectively.

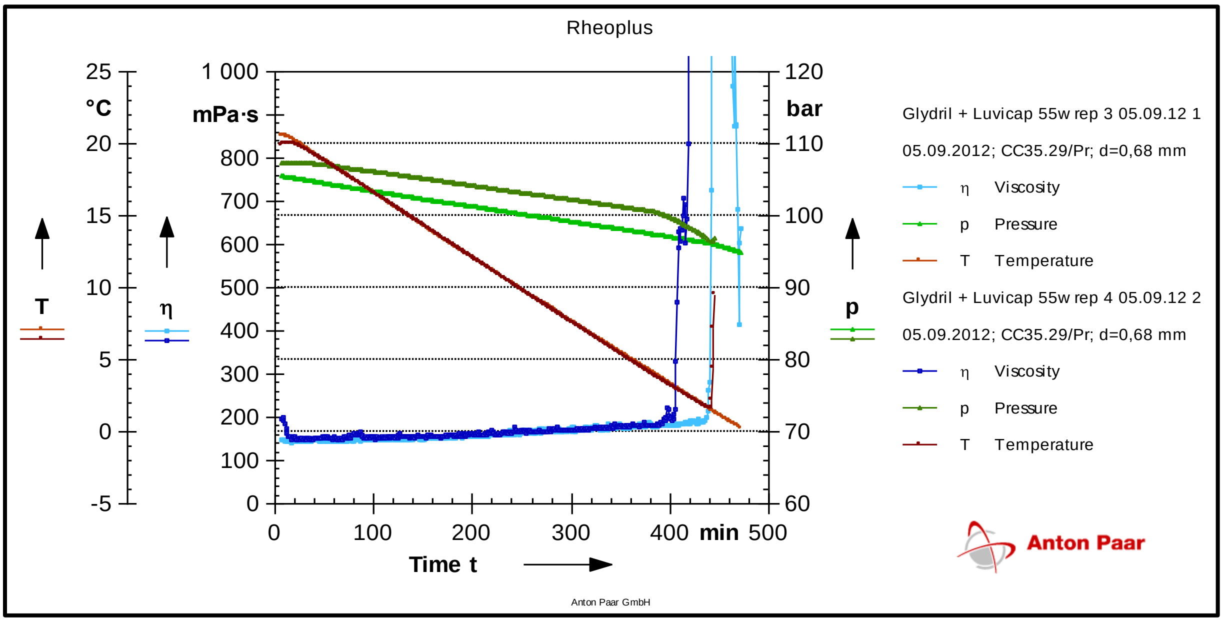


Figure 34: Parallel $3L_{6000}$ (light blue) and $4L_{6000}$ (dark blue) – Constant cooling rate tests on Glydril 1,1SG base fluid with 6000ppm of Luvicap 55w. The graphs show hydrate formation at 1,7°C and 3,0°C respectively.

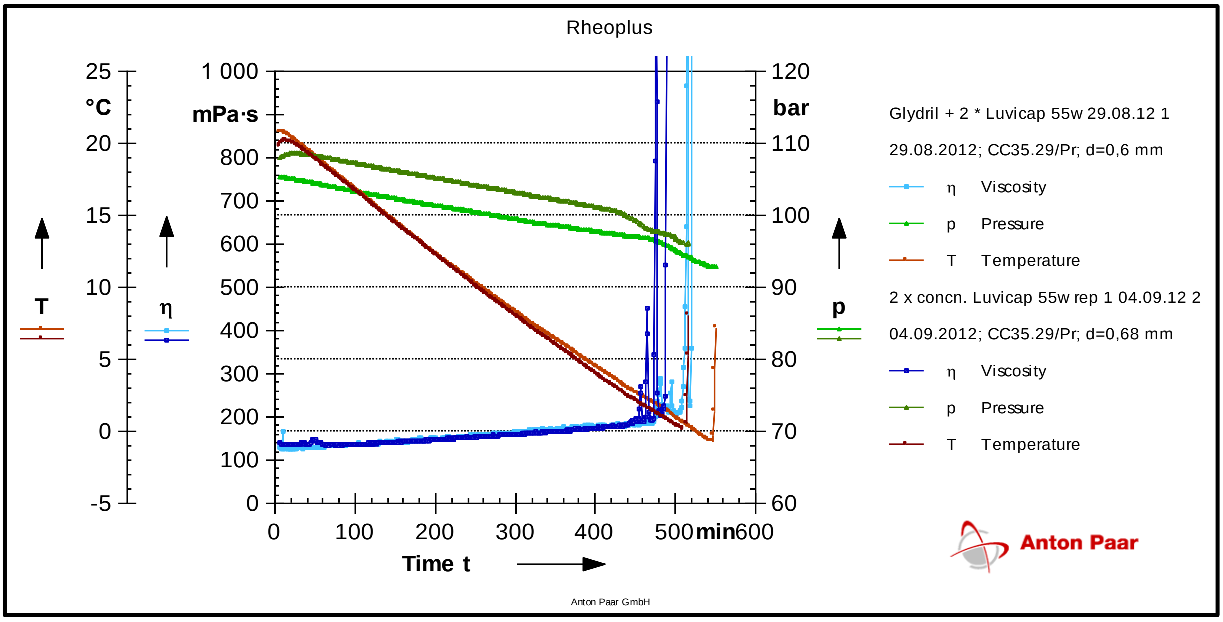


Figure 35: Parallel 1L$_{12000}$ (light blue) and 2L$_{12000}$ (dark blue) – Constant cooling rate tests on Glydril 1,1SG base fluid with 12000ppm of Luvicap 55w. The graphs show hydrate formation at 1,8°C and 1,8°C respectively.

Table 16: Overview of results of constant cooling rate tests on Glydril 1,1SG base fluid with different concentrations of Luvicap 55w.

Test date	Additive and amount to Glydril 1,1SG	Parallel	Hydrate formation temperature (°C)	Average (°C)
16.08.2012	Luvicap 55w (6000ppm)	1L$_{6000}$	2,0	
03.09.2012	Luvicap 55w (6000ppm)	2L$_{6000}$	3,3	
05.09.2012	Luvicap 55w (6000ppm)	3L$_{6000}$	1,7	
05.09.2012	Luvicap 55w (6000ppm)	4L$_{6000}$	3,0	2,5
29.08.2012	Luvicap 55w (12000ppm)	1L$_{12000}$	1,8	
04.09.2012	Luvicap 55w (12000ppm)	2L$_{12000}$	1,8	1,8

4.4 Base fluid with surfactants – Constant cooling rate tests

The following subchapters show the results of the constant cooling rate tests on Glydril 1,1SG base fluid with the various types and concentrations of surfactants.

4.4.1 Base fluid with Arquad 12-30

Figure 37 shows two parallel results ($1A_{6000}$ and $2A_{6000}$) of constant cooling rate tests on Glydril 1,1SG base fluid with the addition of 6000ppm Arquad 12-30 which is a cationic surfactant. The figure shows hydrate formation at 6,2°C and 5,7°C respectively at about 100 bar. The average hydrate formation temperature was thus 6,0°C. Figure 38 shows two parallel results ($1A_{12000}$ and $2A_{12000}$) of constant cooling rate tests on Glydril 1,1SG base fluid with the addition of 12000ppm Arquad 12-30. The figure shows hydrate formation at 7,0°C and 7,0°C respectively at about 100bar. The average hydrate formation temperature was thus 7,0°C. An overview of results is shown in table 17.

Like many surfactants, Arquad 12-30 is a foaming agent. After 5 minutes of mixing on Hamilton Beach about 8 drops of defoamer (EMI 1705) had to be added due to a lot of small air bubbles. A few more drops needed to be added towards the end as a high content of air bubbles in the mud would affect the test volume and hence affect the test results.

Arquad 12-30 has a fish-like odor which disappears when it is mixed into the mud. The substance is not irritating.

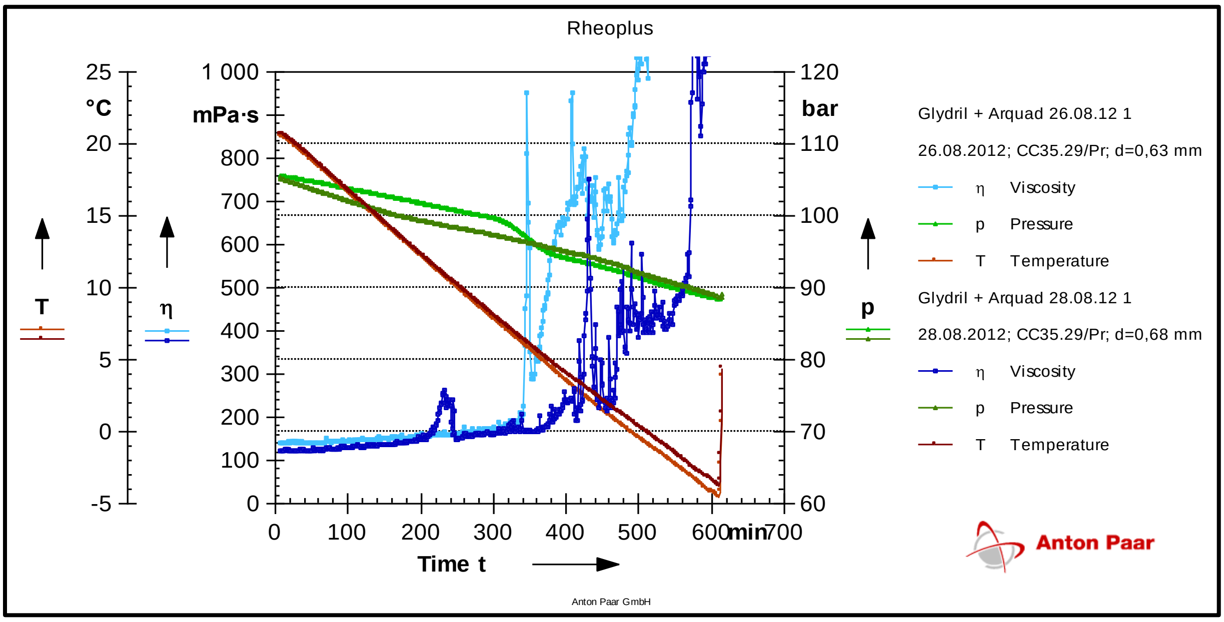


Figure 36: Parallel $1A_{6000}$ (light blue) and $2A_{6000}$ (dark blue) – Constant cooling rate tests on Glydril 1,1SG base fluid with 6000ppm of Arquad 12-30. The graphs show hydrate formation at 6,2°C and 5,7°C respectively.

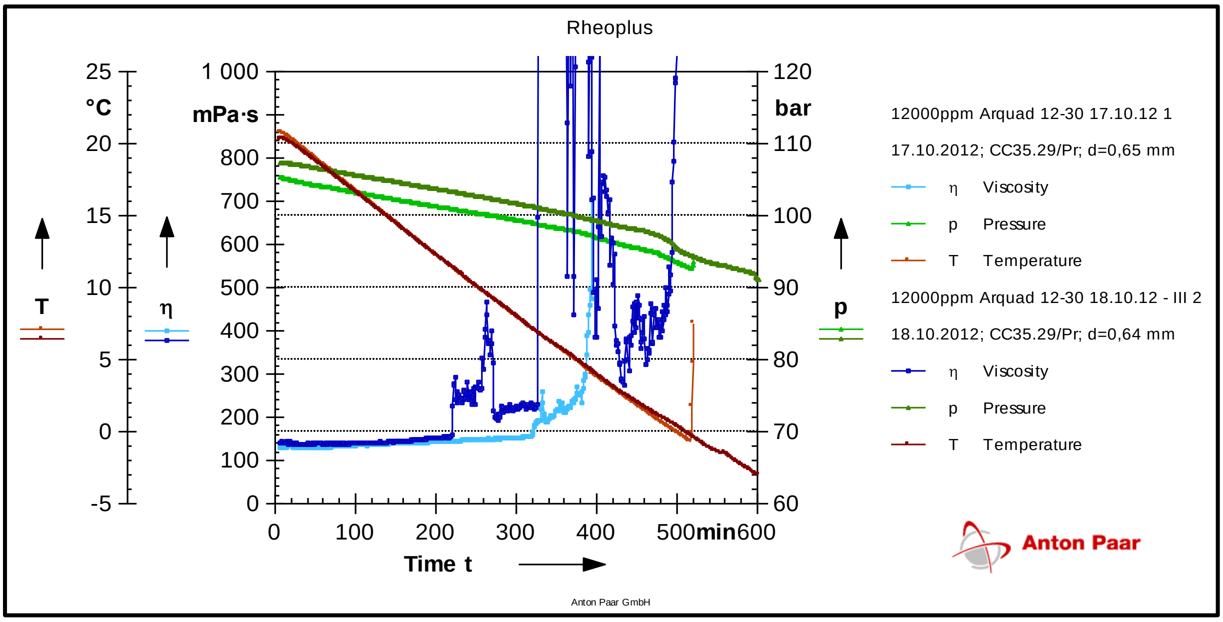


Figure 37: Parallel $1A_{12000}$ (light blue) and $2A_{12000}$ (dark blue) – Constant cooling rate tests on Glydril 1,1SG base fluid with 12000ppm of Arquad 12-30. The graphs show hydrate formation at 7,0°C and 7,0°C respectively.

Table 17: Overview of results of constant cooling rate tests on Glydril 1,1SG base fluid with different concentrations of Arquad 12-30.

Test date	Additive and amount to Glydril 1,1SG	Parallel	Hydrate formation temperature (°C)	Average (°C)
26.08.2012	Arquad 12-30 (6000ppm)	$1A_{6000}$	6,2	
28.08.2012	Arquad 12-30 (6000ppm)	$2A_{6000}$	5,7	6,0
17.10.2012	Arquad 12-30 (12000ppm)	$1A_{12000}$	7,0	
18.10.2012	Arquad 12-30 (12000ppm)	$2A_{12000}$	7,0	7,0

4.4.2 Base fluid with SDS

Figure 39 shows two parallel results ($1S_{6000}$ and $2S_{6000}$) of constant cooling rate tests on Glydril 1,1SG base fluid with the addition of 6000ppm SDS-solution which is an anionic surfactant. The figure shows hydrate formation at 8,2°C and 8,4°C respectively at about 100 bar. The average hydrate formation temperature was thus 8,3°C. Figure 40 shows two parallel results ($1S_{12000}$ and $2S_{12000}$) of constant cooling rate tests on Glydril 1,1SG base fluid with the addition of 12000ppm SDS-solution. The figure shows hydrate formation at 11,9°C and 10,4°C respectively at about 100bar. The average hydrate formation temperature was thus 11,2°C. An overview of results is shown in table 18.

SDS created half the amount of foam that Arquad 12-30 did. The small air bubbles disappeared after 5-15 minutes and no defoamer had to be added. Mixing needed to be performed in a fume hood as SDS is very irritating to eyes, nose and throat even though it is almost odorless.

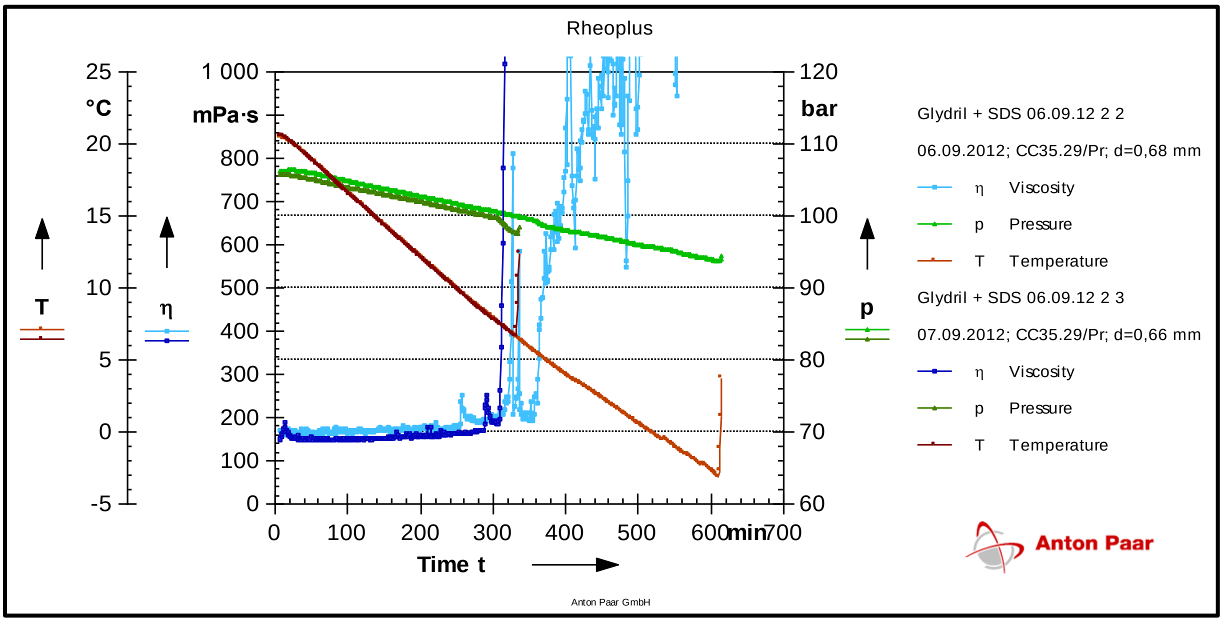


Figure 38: Parallel $1S_{6000}$ (light blue) and $2S_{6000}$ (dark blue) – Constant cooling rate tests on Glydril 1,1SG base fluid with 6000ppm of SDS-solution. The graphs show hydrate formation at 8,2°C and 8,4°C respectively.

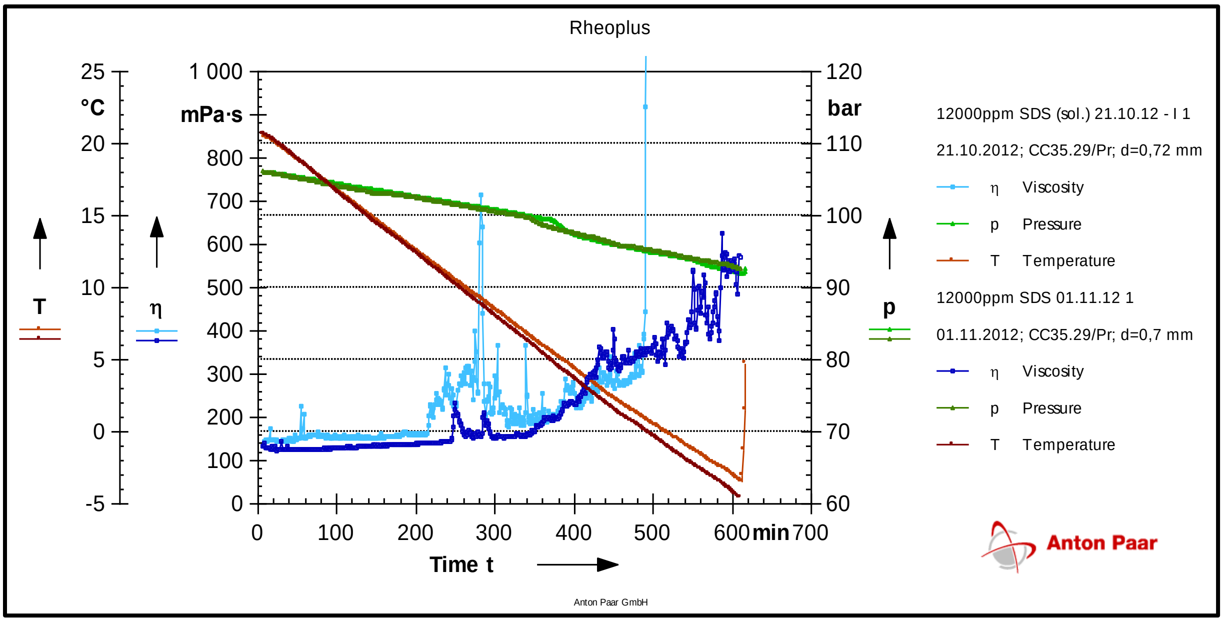


Figure 39: Parallel $1S_{12000}$ (light blue) and $2S_{12000}$ (dark blue) – Constant cooling rate tests on Glydril 1,1SG base fluid with 12000ppm of SDS-solution. The graphs show hydrate formation at 11,9°C and 10,4°C respectively.

Table 18: Overview of results of constant cooling rate tests on Glydril 1,1SG base fluid with different concentrations of SDS-solution.

Test date	Additive and amount to Glydril 1,1SG	Parallel	Hydrate formation temperature (^oC)	Average (^oC)
06.09.2012	SDS (6000ppm)	$1S_{6000}$	8,2	
07.09.2012	SDS (6000ppm)	$2S_{6000}$	8,4	8,3
21.10.2012	SDS (12000ppm)	$1S_{12000}$	11,9	
01.11.2012	SDS (12000ppm)	$2S_{12000}$	10,4	11,2

4.4.3 Base fluid with Aromox C/12-W

Figure 41 shows the results ($1Am_{12000}$ and $2Am_{12000}$) of constant cooling rate test on Glydril 1,1SG base fluid with the addition of 12000ppm Aromox C/12-W, an amine-oxide which is non-ionic due to the alkaline base fluid. The figure shows hydrate formation at 8,4^{o}C and 8,7^{o}C respectively at about 100 bar. The average hydrate formation temperature was thus 8,6^{o}C. An overview of results is shown in table 19.

As Aromox C/12-W created a lot of foam (about twice as much as Arquad 12-30) and the mud foamed over the edge of the mixing cup when mixed, defoamer needed to be added. Although many drops were added (almost 30) the foam did not disappear much. Since this mix could not be used for practical reasons in the field, and because proper results were difficult to obtain due to the foaming, a test of 6000ppm Aromox C/12-W was not performed. In addition, Imbentin-AG/124S/040 which is a non-ionic surfactant was to be tested next, and was thought to have some of the same properties as Aromox C/12-W due to the similar surface charge in the mud.

Aromox C/12-W is almost odorless and not irritating.

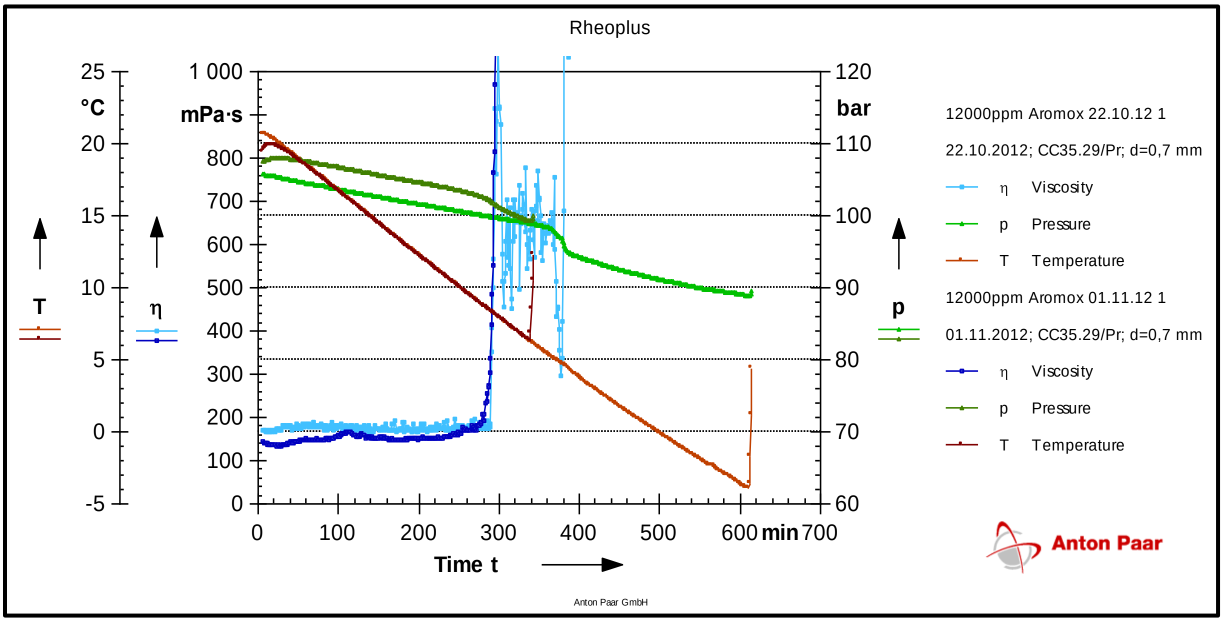


Figure 40: Parallel 1Am$_{12000}$ (light blue) and 2Am$_{12000}$ (dark blue) – Constant cooling rate tests on Glydril 1,1SG base fluid with 12000ppm of Aromox C/12-W. The graphs show hydrate formation at 8,4°C and 8,7°C respectively.

Table 19: Overview of results of constant cooling rate tests on Glydril 1,1SG base fluid with 12000ppm of Aromox C/12-W.

Test date	Additive and amount to Glydril 1,1SG	Parallel	Hydrate formation temperature (°C)	Average (°C)
22.10.2012	Aromox C/12-W (12000ppm)	1Am$_{12000}$	8,4	
01.11.2012	Aromox C/12-W (12000ppm)	2Am$_{12000}$	8,7	8,6

4.4.4 Base fluid with Imbentin-AG/124S/040

Figure 42 shows two parallel results (1I$_{6000}$ and 2I$_{6000}$) of constant cooling rate tests on Glydril 1,1SG base fluid with the addition of 6000ppm Imbentin-AG/124S/040 which is a non-ionic surfactant. The figure shows hydrate formation at 7,0°C and 7,0°C respectively at about 100 bar. The average hydrate formation temperature was thus 7,0°C. Figure 43 shows two parallel results of (1I$_{12000}$ and 2I$_{12000}$) of constant cooling rate tests on Glydril 1,1SG base fluid with the addition of 12000ppm Imbentin-AG/124S/040. The figure shows hydrate formation at 10,9°C and 10,3°C respectively at about 100bar. The average hydrate formation temperature was thus 10,6°C. An overview of results is shown in table 20.

Imbentin-AG/124S/040 did not create a lot of foam and hence no defoamer needed to be added. The foam disappeared after a few minutes. This substance has a strong smell which stings in eyes, nose and throat.

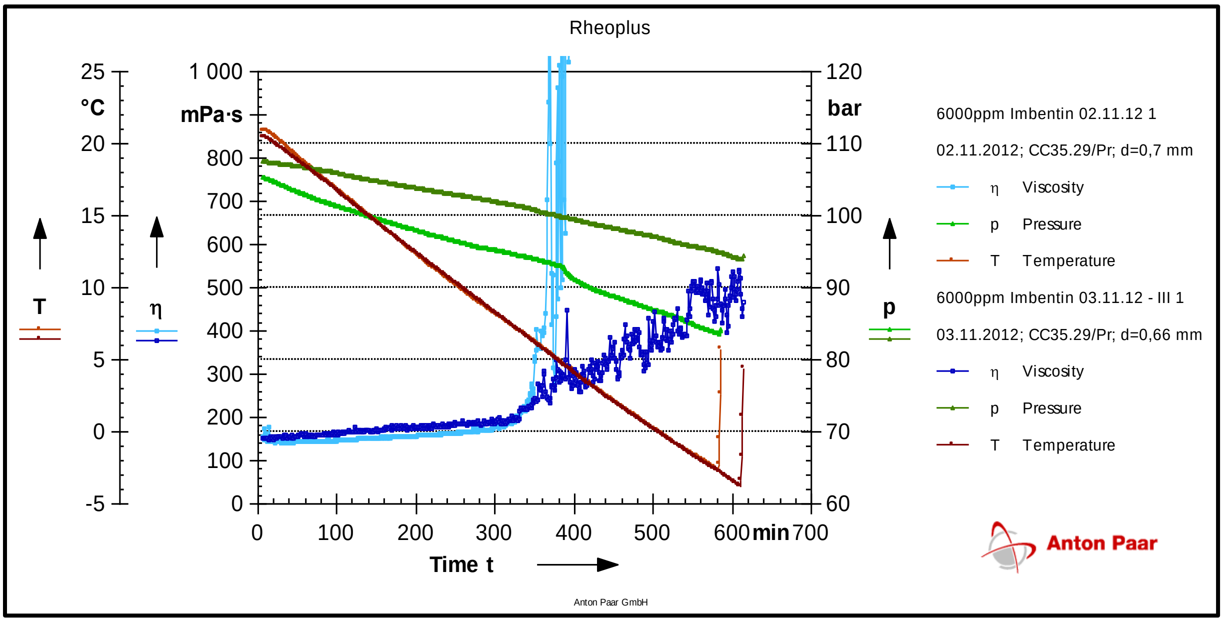


Figure 41: Parallel $1I_{6000}$ (light blue) and $2I_{6000}$ (dark blue) – Constant cooling rate tests on Glydril 1,1SG base fluid with 6000ppm of Imbentin-AG/124S/040. The graphs show hydrate formation at 7,0°C and 7,0°C respectively.

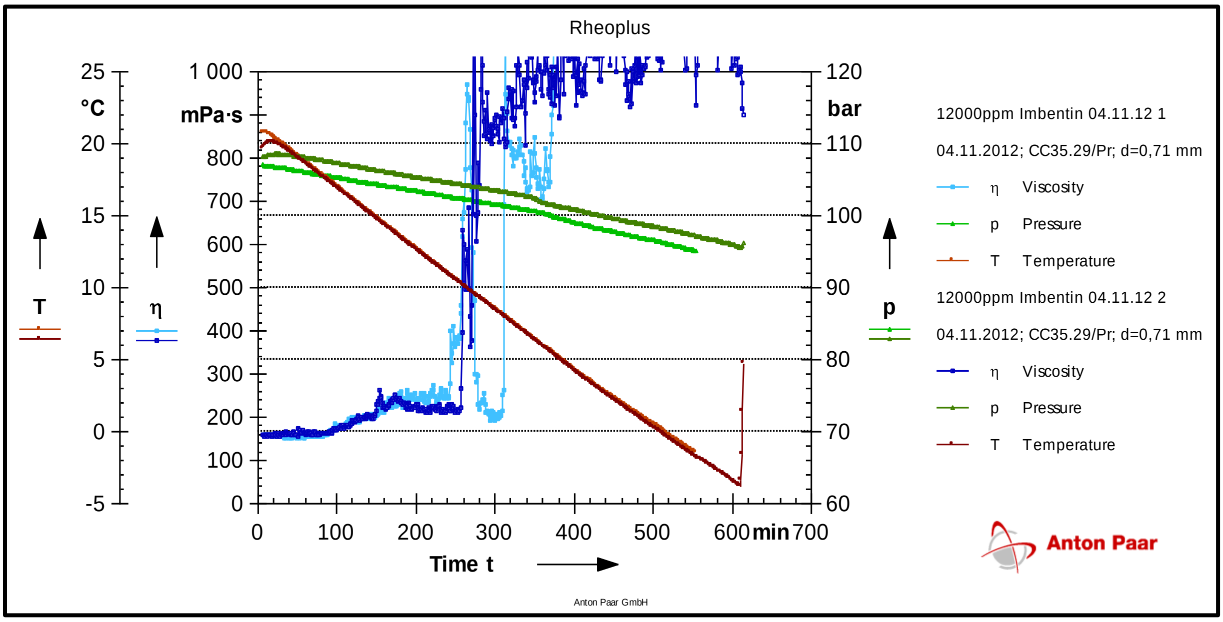


Figure 42: Parallel $1I_{12000}$ (light blue) and $2I_{12000}$ (dark blue) – Constant cooling rate tests on Glydril 1,1SG base fluid with 12000ppm of Imbentin-AG/124S/040. The graphs show hydrate formation at 10,9°C and 10,3°C respectively.

Table 20: Overview of results of constant cooling rate tests on Glydril 1,1SG base fluid with different concentrations of Imbentin-AG/124S/040.

Test date	Additive and amount to Glydril 1,1SG	Parallel	Hydrate formation temperature (^oC)	Average (^oC)
02.11.2012	Imbentin-AG/124S/040 (6000ppm)	$1I_{6000}$	7,0	
03.11.2012	Imbentin-AG/124S/040 (6000ppm)	$2I_{6000}$	7,0	7,0
04.11.2012	Imbentin-AG/124S/040 (12000ppm)	$1I_{12000}$	10,9	
04.11.2012	Imbentin-AG/124S/040 (12000ppm)	$2I_{12000}$	10,3	10,6

4.5 Base fluid with KHI and surfactants/anti-agglomerants – Constant cooling rate tests

The following subchapters show the results of the constant cooling rate tests on Glydril 1,1SG base fluid with KHI together with the various types and concentrations of surfactants/anti-agglomerants.

4.5.1 Base fluid with Luvicap 55w and Arquad 12-30

Figure 44 shows two parallel results ($1L_{6000}A_{6000}$ and $2L_{6000}A_{6000}$) of constant cooling rate tests on Glydril 1,1SG base fluid with the addition of 6000ppm Luvicap 55w and 6000ppm Arquad 12-30. The figure shows hydrate formation at -3,7^oC and -3,0^oC respectively at about 100 bar. The average hydrate formation temperature was thus -3,4^oC. As this was a very good result, additional tests with other concentrations was performed.

The reverse order test results, where 6000ppm Luvicap 55w was added to the base fluid prior to Arquad 12-30 are shown in figure 45. The two parallels ($1RL_{6000}A_{6000}$ and $2RL_{6000}A_{6000}$) shows hydrate formation at 0,6^oC and -1,2^oC at about 100bar, and thus an average hydrate formation temperature of -0,3^oC.

Figure 46 shows two parallel results ($1L_{9000}A_{3000}$ and $2L_{9000}A_{3000}$) of constant cooling rate tests on Glydril 1,1SG base fluid with the addition of 9000ppm Luvicap 55w and 3000ppm Arquad 12-30. The figure shows hydrate formation at 2,8^oC and 0,5^oC respectively at about 100bar. The average hydrate formation temperature was thus 1,7^oC. Figure 47 shows two parallel results ($1L_{3000}A_{9000}$ and $2L_{3000}A_{9000}$) of constant cooling rate tests on Glydril 1,1SG base fluid with the addition of 3000ppm Luvicap 55w and 9000ppm Arquad 12-30. The figure shows hydrate formation at -0,5^oC and 0,1^oC respectively at about 100bar. The average hydrate formation temperature was thus -0,2^oC. Figure 48 shows two parallel results ($1L_{7000}A_{5000}$ and $2L_{7000}A_{5000}$) of constant cooling rate tests on Glydril 1,1SG base fluid with the addition of 7000ppm Luvicap 55w and 5000ppm Arquad 12-30. The figure shows hydrate formation at 1,5^oC and 0,5^oC respectively at about 100bar. The average hydrate formation temperature was thus 1,0°C. Figure 49 shows two parallel results ($1L_{5000}A_{7000}$ and $2L_{5000}A_{7000}$) of constant cooling rate tests on Glydril 1,1SG base fluid with the addition of 5000ppm Luvicap 55w and 7000ppm Arquad 12-30. The figure shows hydrate formation at 1,6°C and -1,5°C respectively at about 100bar. The average hydrate formation temperature was thus 0,1°C.

An overview of results is shown in table 21 and in figure 50. The figure is based on calculated average additional subcooling values obtained from the tests (7,2°C which was the average hydrate formation value for the base fluid – the average hydrate formation temperature of the samples).

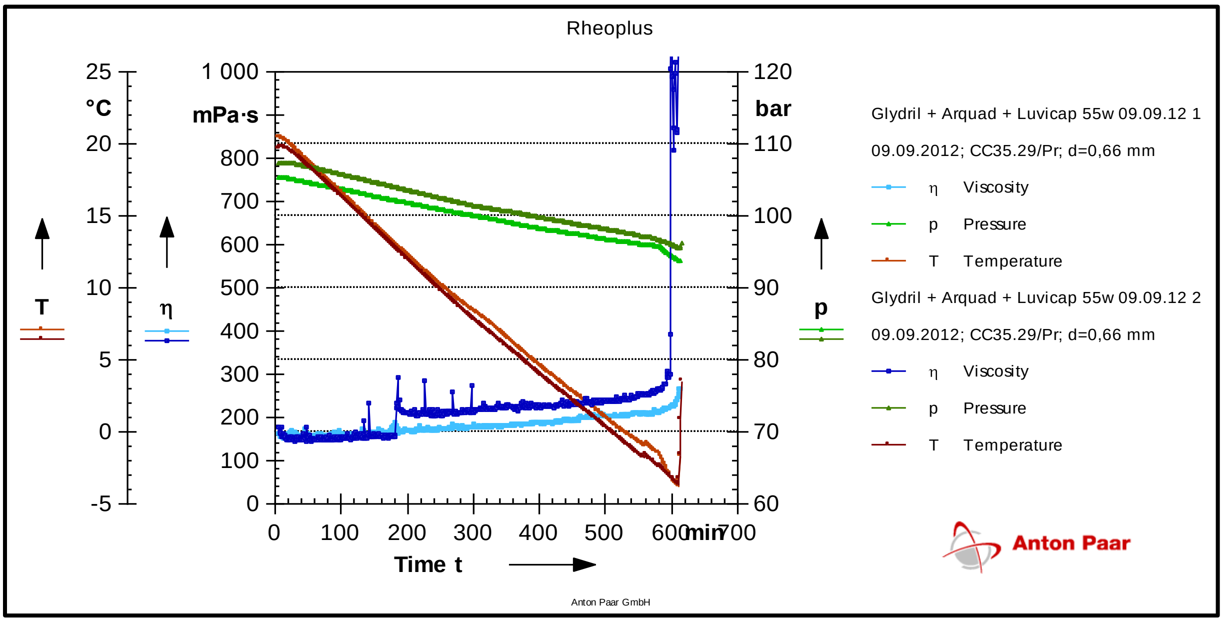


Figure 43: Parallel $1L_{6000}A_{6000}$ (light blue) and $2L_{6000}A_{6000}$ (dark blue) - Constant cooling rate tests on Glydril 1,1SG base fluid with 6000ppm of Luvicap 55w and 6000ppm of Arquad 12-30. The graphs show hydrate formation at -3,7°C and -3,0°C respectively.

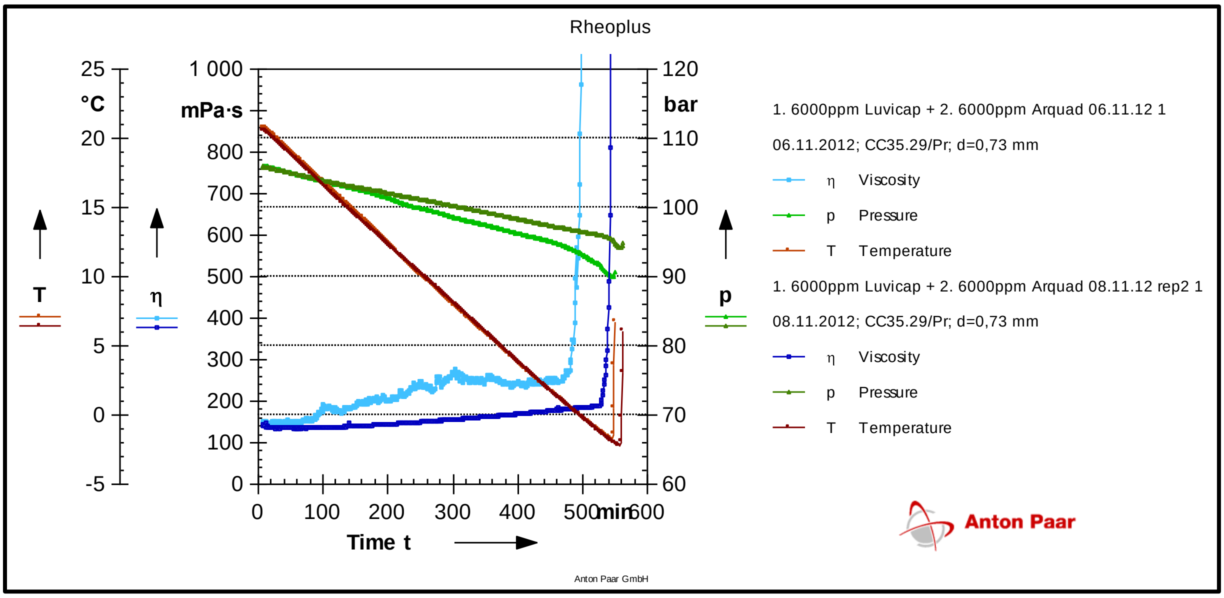


Figure 44: Parallel 1RL$_{6000}$A$_{6000}$ (light blue) and 2RL$_{6000}$A$_{6000}$ (dark blue) – Constant cooling rate tests on Glydril 1,1SG base fluid with 6000ppm of Luvicap 55w prior to 6000ppm of Arquad 12-30. The graphs show hydrate formation at 0,6°C and -1,2°C respectively.

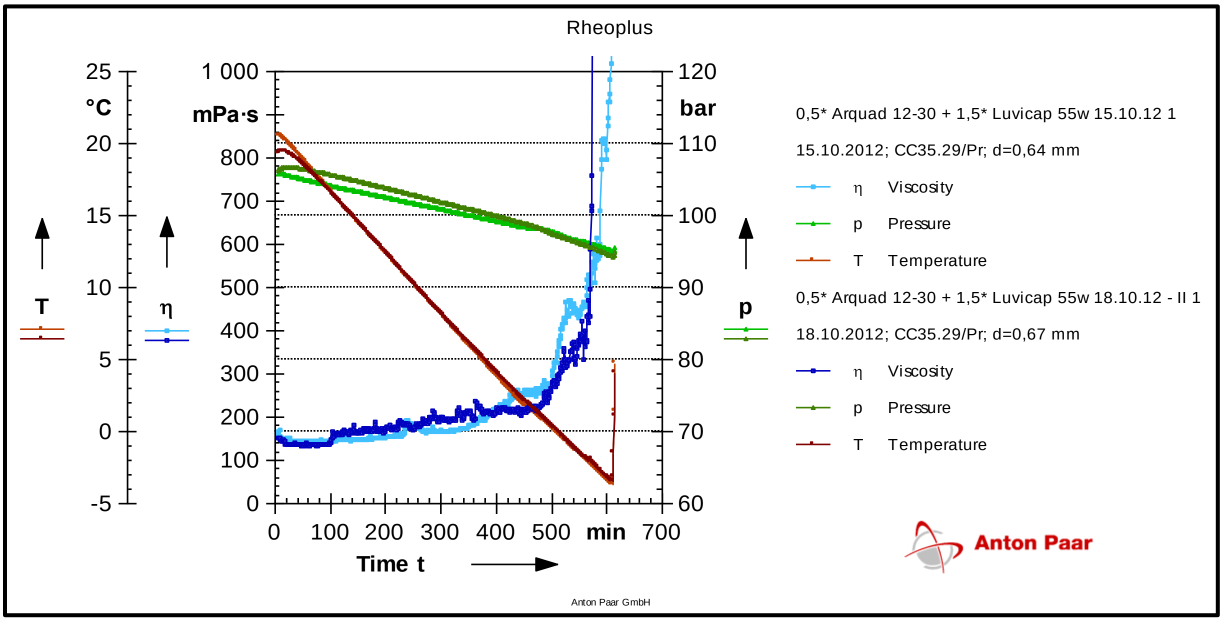


Figure 45: Parallel 1L$_{9000}$A$_{3000}$ (light blue) and 2L$_{9000}$A$_{3000}$ (dark blue) – Constant cooling rate tests on Glydril 1,1SG base fluid with 9000ppm of Luvicap 55w and 3000ppm of Arquad 12-30. The graphs show hydrate formation at 2,8°C and 0,5°C respectively.

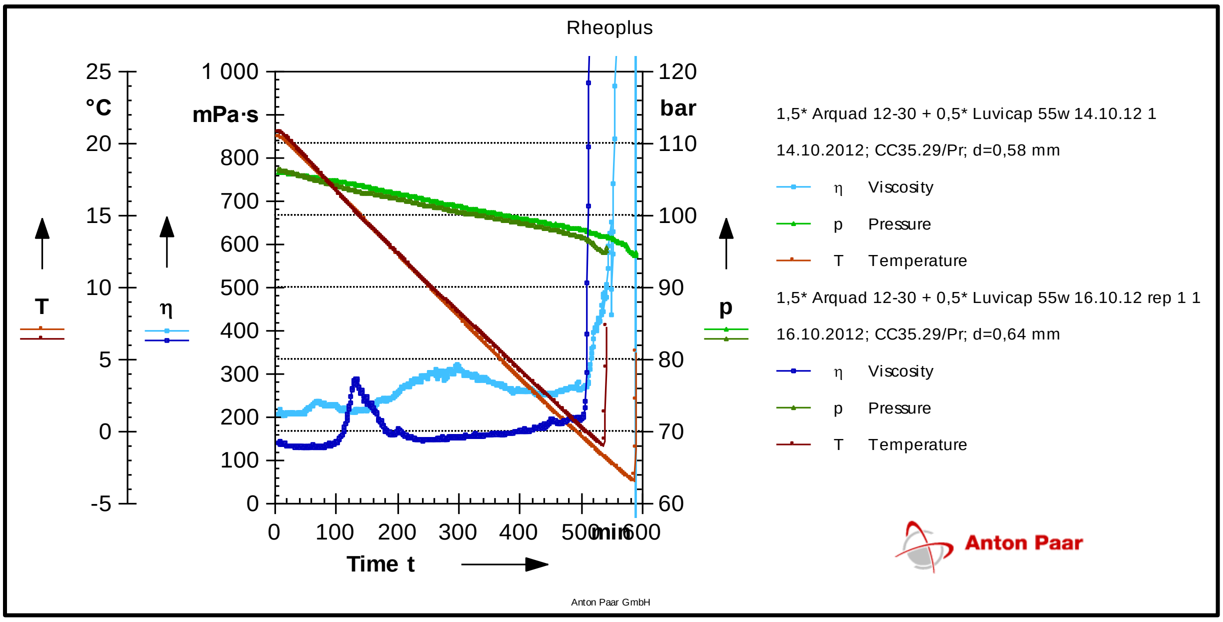


Figure 46: Parallel $1L_{3000}A_{9000}$ (light blue) and $2L_{3000}A_{9000}$ (dark blue) – Constant cooling rate tests on Glydril 1,1SG base fluid with 3000ppm of Luvicap 55w and 9000ppm of Arquad 12-30. The graphs show hydrate formation at -0,5°C and 0,1°C respectively.

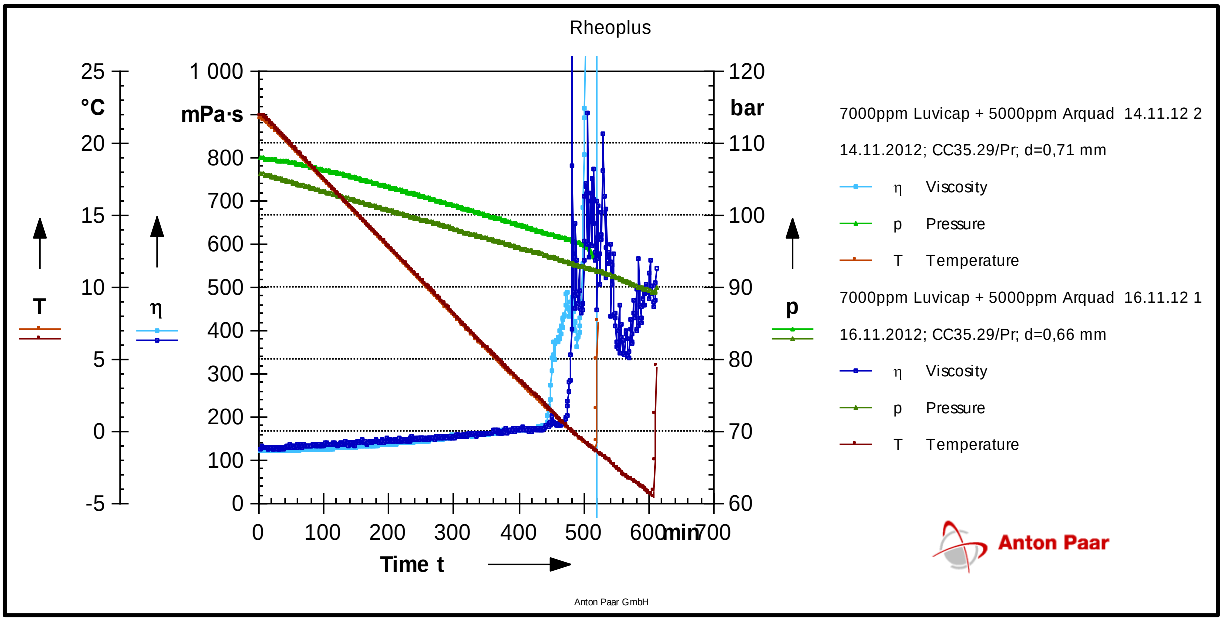


Figure 47: Parallel $1L_{7000}A_{5000}$ (light blue) and $2L_{7000}A_{5000}$ (dark blue) – Constant cooling rate tests on Glydril 1,1SG base fluid with 7000ppm of Luvicap 55w and 5000ppm of Arquad 12-30. The graphs show hydrate formation at 1,5°C and 0,5°C respectively.

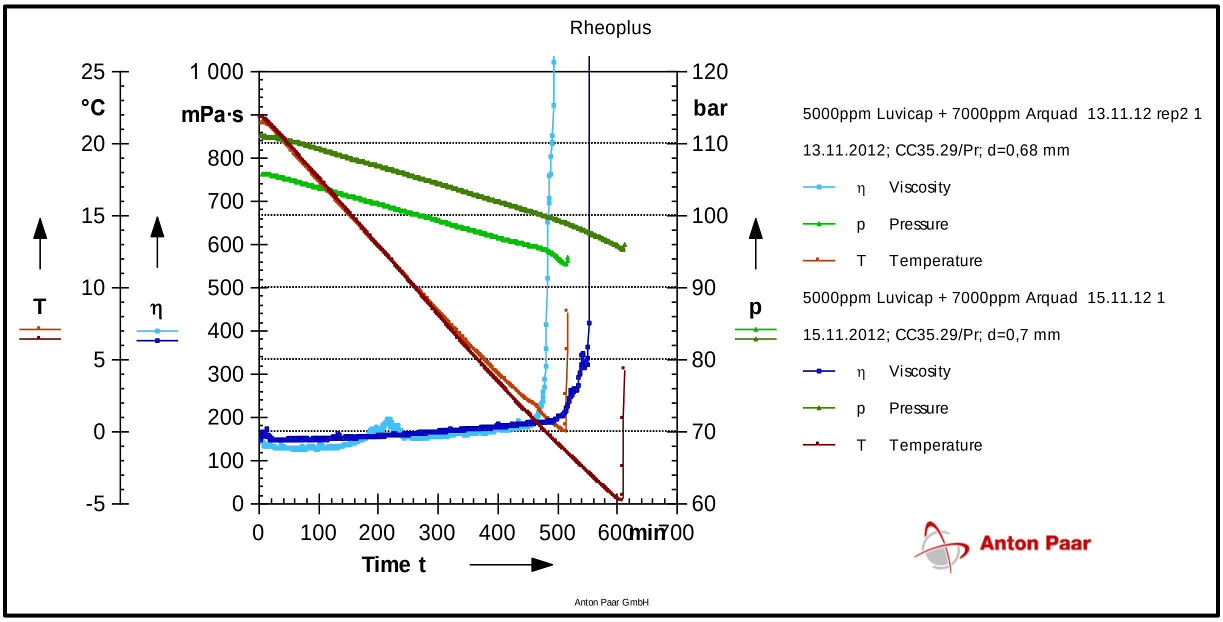


Figure 48: Parallel $1L_{5000}A_{7000}$ (light blue) and $2L_{5000}A_{7000}$ (dark blue) – Constant cooling rate tests on Glydril 1,1SG base fluid with 5000ppm of Luvicap 55w and 7000ppm of Arquad 12-30. The graphs show hydrate formation at 1,6°C and -1,5°C respectively.

Table 21: Overview of results of constant cooling rate tests on Glydril 1,1SG base fluid with different concentrations of Luvicap 55w and Arquad 12-30.

Test date	Additive(s) and amount(s) to Glydril 1,1SG	Parallel	Hydrate formation temperature (°C)	Average (°C)
09.09.2012	Arquad 12-30 (6000ppm) + Luvicap 55w (6000ppm)	$1L_{6000}A_{6000}$	-3,7	
09.09.2012	Arquad 12-30 (6000ppm) + Luvicap 55w (6000ppm)	$2L_{6000}A_{6000}$	-3,0	-3,4
06.11.2012	Luvicap 55w (6000ppm) + Arquad 12-30 (6000ppm) REVERSED!	$1RL_{6000}A_{6000}$	0,6	
08.11.2012	Luvicap 55w (6000ppm) + Arquad 12-30 (6000ppm) REVERSED!	$2RL_{6000}A_{6000}$	-1,2	-0,3
15.10.2012	Arquad 12-30 (3000ppm) + Luvicap 55w (9000ppm)	$1L_{9000}A_{3000}$	2,8	
18.10.2012	Arquad 12-30 (3000ppm) + Luvicap 55w (9000ppm)	$2L_{9000}A_{3000}$	0,5	1,7
14.10.2012	Arquad 12-30 (9000ppm) + Luvicap 55w (3000ppm)	$1L_{3000}A_{9000}$	-0,5	
16.10.2012	Arquad 12-30 (9000ppm) + Luvicap 55w (3000ppm)	$2L_{3000}A_{9000}$	0,1	-0,2
14.11.2012	Arquad 12-30 (5000ppm) + Luvicap 55w (7000ppm)	$1L_{7000}A_{5000}$	1,5	
16.11.2012	Arquad 12-30 (5000ppm) + Luvicap 55w (7000ppm)	$2L_{7000}A_{5000}$	0,5	1,0
13.11.2012	Arquad 12-30 (7000ppm) + Luvicap 55w (5000ppm)	$1L_{5000}A_{7000}$	1,6	
15.11.2012	Arquad 12-30 (7000ppm) + Luvicap 55w (5000ppm)	$2L_{5000}A_{7000}$	-1,5	0,1

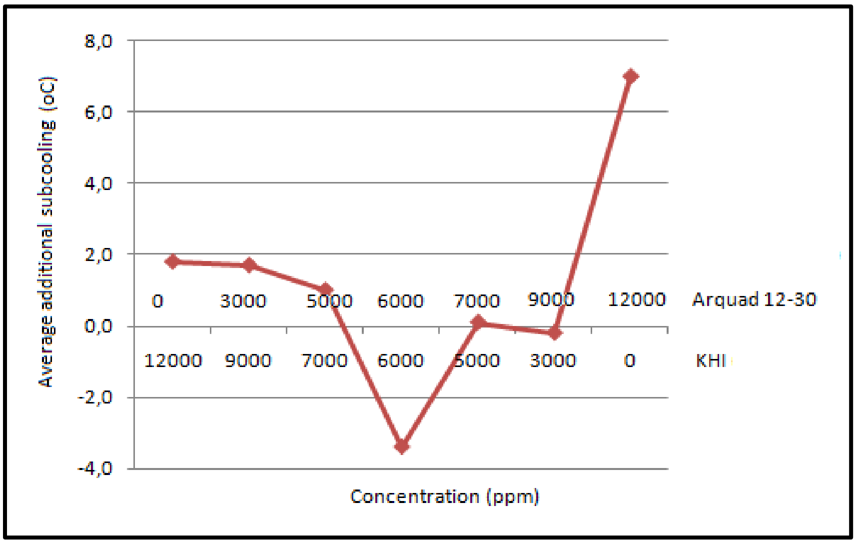


Figure 49: A graphic overview of results of constant cooling rate tests on Glydril 1,1SG base fluid with different concentrations of Luvicap 55w and Arquad 12-30. The graph is based on the average additional subcooling values obtained.

4.5.2 Base fluid with Luvicap 55w and SDS

Figure 51 shows two parallel results ($1L_{6000}S_{6000}$ and $2L_{6000}S_{6000}$) of constant cooling rate tests on Glydril 1,1SG base fluid with the addition of 6000ppm Luvicap 55w and 6000ppm SDS. The figure shows hydrate formation at 4,0°C and 1,5°C respectively at about 100 bar. The average hydrate formation temperature was thus 2,8°C. As this was a poor result compared to the same test with Arquad 12-30, and also because the results showed large variations in formation temperature, further testing with other concentrations was not performed. An overview of results is shown in table 22.

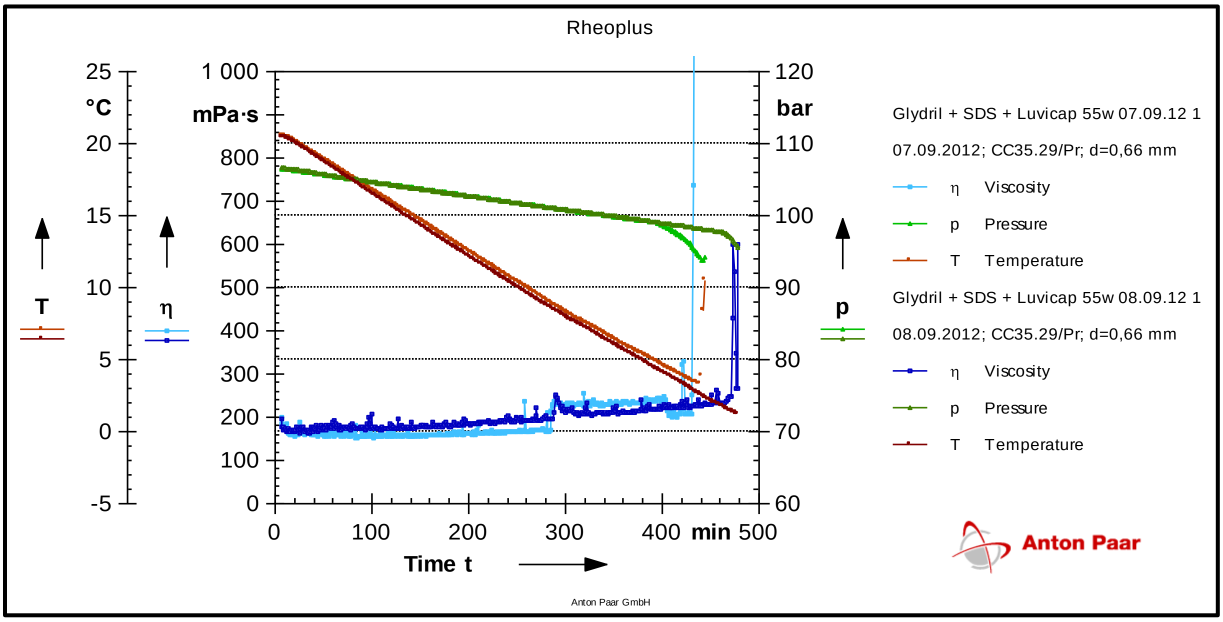


Figure 50: Parallel $1L_{6000}S_{6000}$ (light blue) and $2L_{6000}S_{6000}$ (dark blue) – Constant cooling rate tests on Glydril 1,1SG base fluid with 6000ppm Luvicap 55w and 6000ppm SDS. The graphs show hydrate formation at 4,0°C and 1,5°C respectively.

Table 22: Overview of results of constant cooling rate tests on Glydril 1,1SG base fluid with Luvicap 55w and SDS.

Test date	Additive(s) and amount(s) to Glydril 1,1SG	Parallel	Hydrate formation temperature (°C)	Average (°C)
07.09.2012	SDS (6000ppm) + Luvicap 55w (6000ppm)	$1L_{6000}S_{6000}$	4,0	
08.09.2012	SDS (6000ppm) + Luvicap 55w (6000ppm)	$2L_{6000}S_{6000}$	1,5	2,8

4.5.3 Base fluid with Luvicap 55w and Aromox C/12-W

Figure 52 shows two parallel results ($1L_{6000}Am_{6000}$ and $2L_{6000}Am_{6000}$) of constant cooling rate tests on Glydril 1,1SG base fluid with the addition of 6000ppm Luvicap 55w and 6000ppm Aromox C/12-W. Although this mixture could not be used in the field, the same test was performed as for the other additives to see the effect of this type of surfactant for comparison to the other classes. The figure shows hydrate formation at 2,9°C and 3,5°C respectively at about 100 bar. The average hydrate formation temperature was thus 3,2°C. As this was a poor result compared to the same test with Arquad 12-30, and also due to the poor mud quality and because proper results were difficult to obtain due to the foaming, further testing with other concentrations was not performed. An overview of results is shown in table 23.

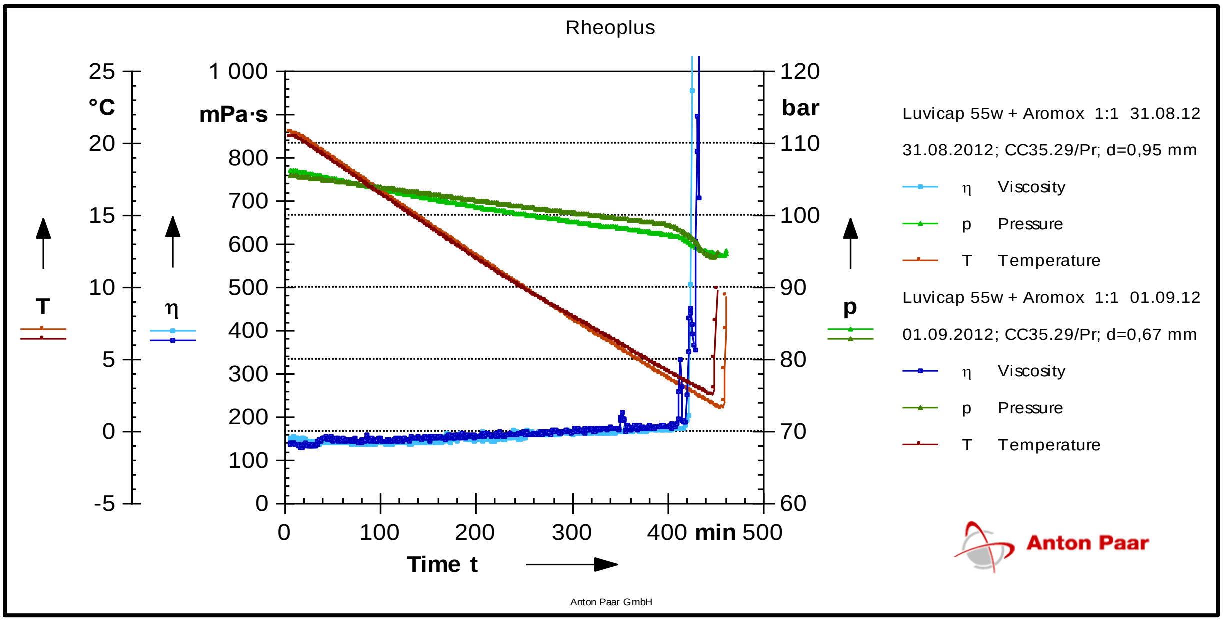


Figure 51: Parallel $1L_{6000}Am_{6000}$ (light blue) and $2L_{6000}Am_{6000}$ (dark blue) – Constant cooling rate tests on Glydril 1,1SG base fluid with 6000ppm Luvicap 55w and 6000ppm Aromox C/12-W. The graphs show hydrate formation at 2,9°C and 3,5°C respectively.

Table 23: Overview of results of constant cooling rate test on Glydril 1,1SG base fluid with Luvicap 55w and Aromox C/12-W.

Test date	Additive(s) and amount(s) to Glydril 1,1SG	Parallel	Hydrate formation temperature (°C)	Average (°C)
31.08.2012	Luvicap 55w (6000ppm) + Aromox C/12-W (6000ppm)	$1L_{6000}Am_{6000}$	2,9	
01.09.2012	Luvicap 55w (6000ppm) + Aromox C/12-W (6000ppm)	$2L_{6000}Am_{6000}$	3,5	3,2

4.5.4 Base fluid with Luvicap 55w and Imbentin-AG/124S/040

Figure 53 shows two parallel results ($1L_{6000}I_{6000}$ and $2L_{6000}I_{6000}$) of constant cooling rate tests on Glydril 1,1SG base fluid with the addition of 6000ppm Luvicap 55w and 6000ppm Imbentin-AG/124S/040. The figure shows hydrate formation at 4,8°C and 4,2°C respectively at about 100 bar. The average hydrate formation temperature was thus 4,5°C. As this was a poor result compared to the same test with Arquad 12-30, further testing with other concentrations was not performed. An overview of results is shown in table 24.

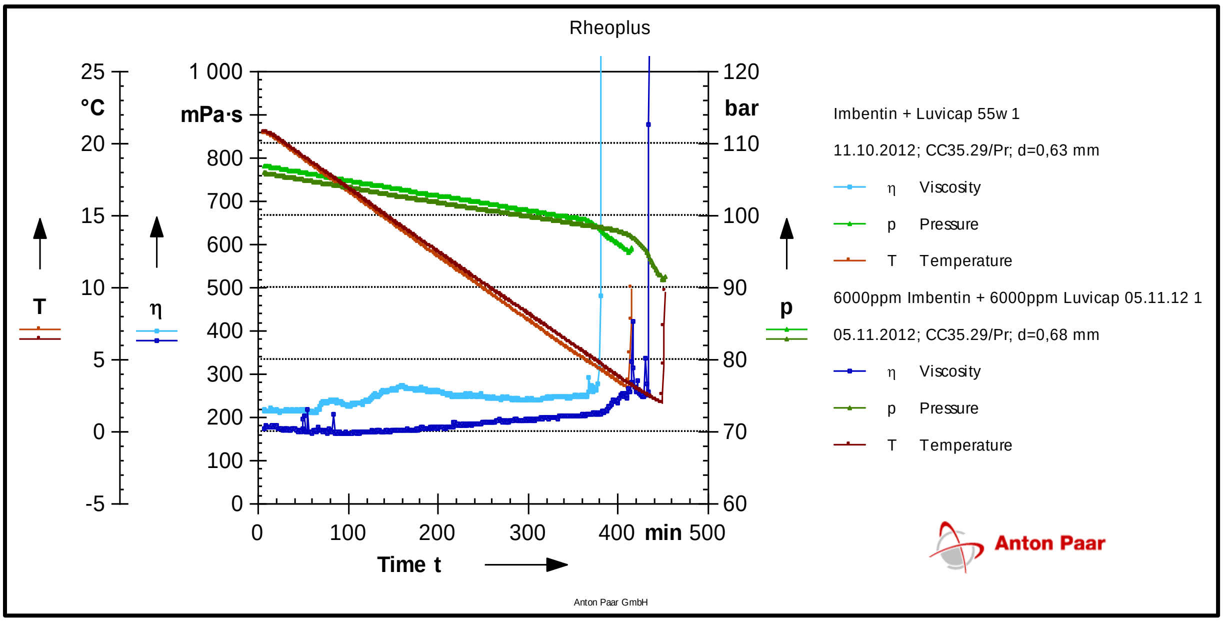


Figure 52: Parallel $1L_{6000}l_{6000}$ (light blue) and $2L_{6000}l_{6000}$ (dark blue) – Constant cooling rate tests on Glydril 1,1SG base fluid with 6000ppm of Luvicap 55w and 6000ppm Imbentin-AG/124S/040. The graphs show hydrate formation at 4,8^{o}C and 4,2^{o}C respectively.

Table 24: Overview of results of constant cooling rate tests on Glydril 1,1SG base fluid with Luvicap 55w and Imbentin-AG/124S/040.

Test date	Additive(s) and amount(s) to Glydril 1,1SG	Parallel	Hydrate formation temperature (^{o}C)	Average (^{o}C)
11.10.2012	Imbentin-AG/124S/040 (6000ppm) + Luvicap 55w (6000ppm)	$1L_{6000}l_{6000}$	4,8	
05.11.2012	Imbentin-AG/124S/040 (6000ppm) + Luvicap 55w (6000ppm)	$2L_{6000}l_{6000}$	4,2	4,5

4.5.5 Base fluid with Luvicap 55w and the special designed anti-agglomerants

Figure 54 shows the results $1L_{6000}151_{6000}$ and $2L_{6000}445_{6000}$ of constant cooling rate tests on Glydril 1,1SG base fluid with the addition of 6000ppm Luvicap 55w and 6000ppm Cdld-151/6000ppm Cdld-445 respectively. The figure shows hydrate formation at 5,7^{o}C and 5,7^{o}C respectively at about 100 bar. The average hydrate formation temperature was thus 5,7^{o}C. As this was a poor result compared to the same test with Arquad 12-30, further testing with other concentrations was not performed. An overview of results is shown in table 25.

Cdld-151 and Cdld-445 has a sweet smell and presented no foaming when mixed. These substances are irritating to nose and throat.

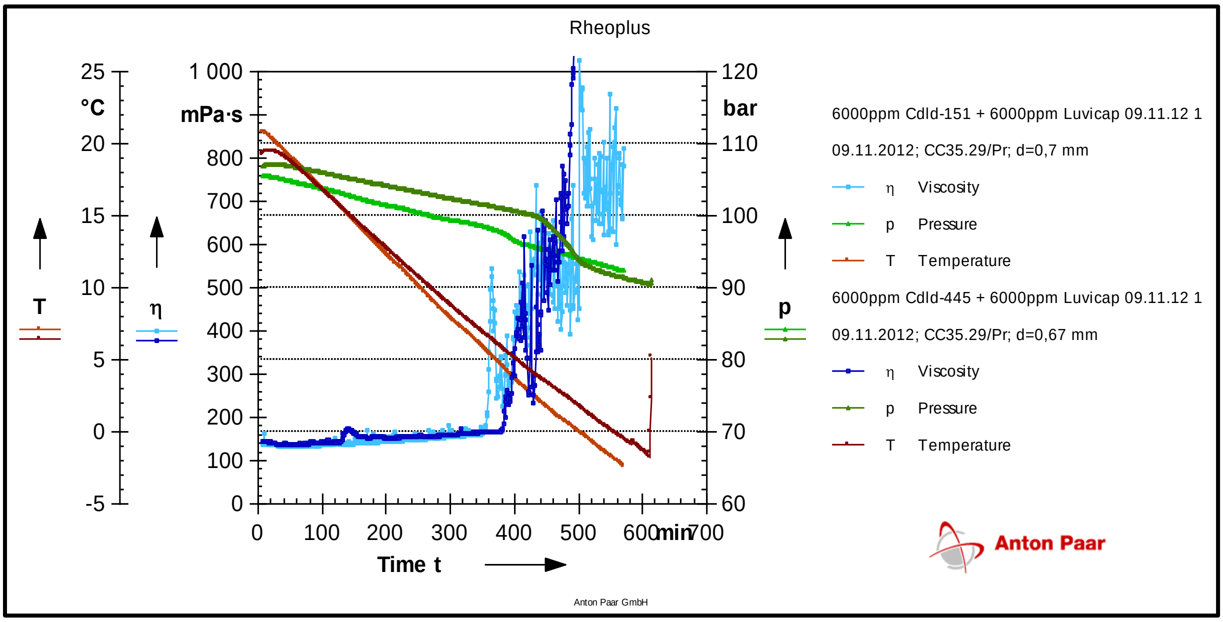


Figure 53: Results of samples $1L_{6000}151_{6000}$ (light blue) and $2L_{6000}445_{6000}$ (dark blue) – Constant cooling rate tests on Glydril 1,1SG base fluid with 6000ppm of Luvicap 55w and 6000ppm Cdld-151 /6000ppm Cdld-445. The graphs show hydrate formation at 5,7°C and 5,7°C respectively.

Table 25: Overview of results of constant cooling rate tests on Glydril 1,1SG base fluid with Luvicap 55w and Cdld-151/Cdld-445.

Test date	Additive(s) and amount(s) to Glydril 1,1SG	Parallel	Hydrate formation temperature (°C)
09.11.2012	Cdld-151 (6000ppm) + Luvicap 55w (6000ppm)	$1L_{6000}151_{6000}$	5,7
09.11.2012	Cdld-445 (6000ppm) + Luvicap 55w (6000ppm)	$1L_{6000}445_{6000}$	5,7

4.6 Summary of constant cooling rate tests

Table 26 shows a summary of all the constant cooling rate test results.

Table 26: Overview of results of all constant cooling rate tests.

Test date	Additive(s) and amount(s) to Glydril 1,1SG	Parallel	Hydrate formation temperature (°C)	Average (°C)
16.08.2012		1G	6,7	
01.10.2012		2G	7,6	7,2
16.08.2012	Luvicap 55w (6000ppm)	$1L_{6000}$	2,0	
03.09.2012	Luvicap 55w (6000ppm)	$2L_{6000}$	3,3	
05.09.2012	Luvicap 55w (6000ppm)	$3L_{6000}$	1,7	
05.09.2012	Luvicap 55w (6000ppm)	$4L_{6000}$	3,0	2,5
29.08.2012	Luvicap 55w (12000ppm)	$1L_{12000}$	1,8	
04.09.2012	Luvicap 55w (12000ppm)	$2L_{12000}$	1,8	1,8
26.08.2012	Arquad 12-30 (6000ppm)	$1A_{6000}$	6,2	
28.08.2012	Arquad 12-30 (6000ppm)	$2A_{6000}$	5,7	6,0
17.10.2012	Arquad 12-30 (12000ppm)	$1A_{12000}$	7,0	
18.10.2012	Arquad 12-30 (12000ppm)	$2A_{12000}$	7,0	7,0
06.09.2012	SDS (6000ppm)	$1S_{6000}$	8,2	
07.09.2012	SDS (6000ppm)	$2S_{6000}$	8,4	8,3
21.10.2012	SDS (12000ppm) - Solution	$1S_{12000}$	11,9	
01.11.2012	SDS (12000ppm) - Solution	$2S_{12000}$	10,4	10,2
22.10.2012	Aromox C/12-W (12000ppm)	$1Am_{12000}$	8,4	
01.11.2012	Aromox C/12-W (12000ppm)	$2Am_{12000}$	8,7	8,6
02.11.2012	Imbentin-AG/124S/040 (6000ppm)	$1I_{6000}$	7,0	
03.11.2012	Imbentin-AG/124S/040 (6000ppm)	$2I_{6000}$	7,0	7,0
04.11.2012	Imbentin-AG/124S/040 (12000ppm)	$1I_{12000}$	10,9	
04.11.2012	Imbentin-AG/124S/040 (12000ppm)	$2I_{12000}$	10,3	10,6
09.09.2012	Arquad 12-30 (6000ppm) + Luvicap 55w (6000ppm)	$1L_{6000}A_{6000}$	-3,7	
09.09.2012	Arquad 12-30 (6000ppm) + Luvicap 55w (6000ppm)	$2L_{6000}A_{6000}$	-3	-3,4
06.11.2012	Luvicap 55w (6000ppm) + Arquad 12-30 (6000ppm) REVERSED!	$1RL_{6000}A_{6000}$	0,6	
08.11.2012	Luvicap 55w (6000ppm) + Arquad 12-30 (6000ppm) REVERSED!	$2RL_{6000}A_{6000}$	-1,2	-0,3
15.10.2012	Arquad 12-30 (3000ppm) + Luvicap 55w (9000ppm)	$1L_{9000}A_{3000}$	2,8	
18.10.2012	Arquad 12-30 (3000ppm) + Luvicap 55w (9000ppm)	$2L_{9000}A_{3000}$	0,5	1,7
14.10.2012	Arquad 12-30 (9000ppm) + Luvicap 55w (3000ppm)	$1L_{3000}A_{9000}$	-0,5	
16.10.2012	Arquad 12-30 (9000ppm) + Luvicap 55w (3000ppm)	$2L_{3000}A_{9000}$	0,1	-0,2

14.11.2012	Arquad 12-30 (5000ppm) + Luvicap 55w (7000ppm)	$1L_{7000}A_{5000}$	1,5	
16.11.2012	Arquad 12-30 (5000ppm) + Luvicap 55w (7000ppm)	$2L_{7000}A_{5000}$	0,5	1,0
13.11.2012	Arquad 12-30 (7000ppm) + Luvicap 55w (5000ppm)	$1L_{5000}A_{7000}$	1,6	
15.11.2012	Arquad 12-30 (7000ppm) + Luvicap 55w (5000ppm)	$2L_{5000}A_{7000}$	-1,5	0,1
07.09.2012	SDS (6000ppm) + Luvicap 55w (6000ppm)	$1L_{6000}S_{6000}$	4	
08.09.2012	SDS (6000ppm) + Luvicap 55w (6000ppm)	$2L_{6000}S_{6000}$	1,5	2,8
31.08.2012	Aromox 12-W (6000ppm) + Luvicap 55w (6000ppm)	$1L_{6000}Am_{6000}$	2,9	
01.09.2012	Aromox 12-W (6000ppm) + Luvicap 55w (6000ppm)	$1L_{6000}Am_{6000}$	3,5	3,2
11.10.2012	Imbentin-AG/124S/040 (6000ppm) + Luvicap 55w (6000ppm)	$1L_{6000}I_{6000}$	4,8	
05.11.2012	Imbentin-AG/124S/040 (6000ppm) + Luvicap 55w (6000ppm)	$2L_{6000}I_{6000}$	4,2	4,5
09.11.2012	Cdld-151 (6000ppm) + Luvicap 55w (6000ppm)	$1L_{6000}151_{6000}$	5,7	
09.11.2012	Cdld-445 (6000ppm) + Luvicap 55w (6000ppm)	$1L_{6000}445_{6000}$	5,7	

4.7 WBM compatibility testing

The results of the standard WBM test on Glydril 1,1SG base fluid with the different additives used in the constant cooling rates tests, generally presented small differences compared to the base fluid. Complete results can be found in APPENDIX I with further comments.

5 DISCUSSION

The following sub-chapters describe the results from the constant cooling rate tests. In general, several uncertainties were present during these measurements.

Reasons for slightly dissimilar viscosity graphs and difference in formation temperature between two parallels may have been due to a difference in equipment conditions like more/less worn out ball-bearings or rust, or due to random chemical reactions between the drilling fluid and the additives under the conditions present. In some cases, smaller deviate peaks are present prior to the catastrophic growth. This is probably due to clusters of hydrates, and thus the torque increases for a short period of time. This is seen in several graphs as a number of peaks and dips right next to each other after hydrate formation starts, which represents large tugs and relieves on the measuring cylinder respectively.

Another reason for dissimilar viscosity graphs may have been that the mud was less fresh in some samples, as a big batch was mixed and samples were taken from this. Although the samples were re-mixed as the additives were added, this may have altered the drilling fluid somewhat. This may be indicated by a difference in start-viscosity between two parallels. Differences in start viscosity may also have been due to air bubbles present in the samples. Foaming in the samples will also increase the gas-water interfacial area and thus more rapid nucleation and hydrate formation may occur. All of the surfactants created foam, except for the special designed AA´s. Although defoamer was used, some foam may have been left in the samples and thus higher hydrate formation temperatures were obtained.

Finally, the most important uncertainty in this study is that the measurements were mainly done with two parallels which only provide an indication of the samples´ actual hydrate formation temperatures. Several parallels needs to be conducted as the hydrate formation temperatures may be more widely spread than indicated by these results; hence the average value may be somewhat different. This is indicated by the four parallels measured for 6000ppm Luvicap 55w (figure 34 and 35) in which the hydrate formation temperatures (2,0°C, 3,3°C, 1,7°C and 3,0°C) were fairly spread. Therefore, to know for sure if a combination is better than another, more parallels needs to be conducted. In addition, statistical tests (e.g. a T-test) need to be performed on the results to show how valid the results are.

5.1 Base fluid and base fluid with Luvicap 55w

The parallel results from the constant cooling rate tests on the low inhibited Glydril 1,1SG base fluid (figure 32 and 33) and on the base fluid with Luvicap 55w (figure 34, 35 and 36) presented clear and sudden points of catastrophic hydrate growth. Hydrate formation temperatures were obtained from the points where the viscosity graphs presented a sudden peak and the pressure presented a sudden decrease. Luvicap 55w does not seem to affect the base fluid with respect to these sharp and sudden peaks, which is desirable when used in the field. The hydrate formation is preferred to be sudden and not gradual which as shown for other combinations in the following discussion. Gradual increases present a larger uncertainty, than a sharp and clear point of hydrate formation. The results indicate that the addition of 6000ppm Luvicap 55w will give the base fluid an average additional subcooling of 4,7°C, as the average hydrate formation temperatures for the base fluid and base fluid with Luvicap 55w were 7,2°C and 2,5°C respectively. The variations in hydrate formation temperatures (2,0°C, 3,3°C, 1,7°C and 3,0°C) in addition to the general uncertainties may be a result of a too low dosage of Luvicap 55w; as described in the literature review, the KHI needs to be present at a minimum concentration (based on the amount of water phase) for sufficient performance. It may be random if the KHI is bound to the ice-crystals and/or imitate formers or if it is adsorbed onto surfaces, as both hydrogen bonds between water and KHI and hydrophobic interactions between KHI and particles are of the same strength. If the KHI adsorbs onto surfaces, some inhibition effect will be lost although this removes some nucleation sites. For the KHI to have elevated inhibition performance, a higher dose may stabilize its effect in the water phase. This theory may have been confirmed by the tests with the addition of 12000ppm Luvicap 55w to the base fluid, where both parallel results presented a hydrate formation temperature of 1,8°C. The hydrate formation temperature seems to be more stabilized at this point due to the higher concentration. The 12000ppm addition appears to give the base fluid an additional subcooling of 5,4°C, which is slightly higher than for the 6000ppm addition. These two observations may indicate that all the particles in the sample are "covered" and that the remaining KHI molecules will inhibit the water cages. Another observation is that the formation temperatures obtained from the 12000ppm samples are close to some of those from the 6000ppm samples. This may indicate that an optimal concentration of Luvicap 55w lies between 6000ppm and 12000ppm somewhere, and that this concentration will offer a hydrate formation temperature which is stabilized at around 1,8°C (an additional subcooling of 5,4°C).

5.2 Base fluid with surfactants

The parallel results from the constant cooling rate tests on the Glydril 1,1SG base fluid with the addition of the different types and concentrations of surfactants generally show very unstable hydrate growth. A number of the viscosity graphs are increasing gradually before catastrophic growth is reached, while other viscosity graphs have sharp peaks similar to those of the base fluid and base fluid with KHI. In the cases of gradual growth the hydrate formation temperatures were obtained from the onset, which also serves for the rest of the results. The growth trends appear to be very random and seem to have no connection with type and concentration of surfactant. The surfactants seem to create some kind of instability and randomness. In addition to the general uncertainties, something is clearly happening here in comparison to the base fluid with KHI. The several peaks and dips present after hydrate formation starts in many of the parallels may be due to the surfactants´ adsorbing properties. As the adsorption onto barite particles, onto water molecules and/or onto other constituents of the drilling fluid is a dynamic process, this may be a reason for the several peaks and dips. The surfactants may enter and leave these surfaces or interfaces, which may reduce and increase the hydrate growth respectively before catastrophic growth.

The addition of the cationic surfactant Arquad 12-30 (figure 37 and 38) showed slight variations in hydrate formation temperature for the 6000ppm concentration (6,2^{o}C and 5,7^{o}C), while the 12000ppm concentration parallels presented the same temperature (7,0^{o}C). Differences in parallels are probably due to the general uncertainties. The average hydrate formation temperatures were thus 6,0^{o}C and 7,0^{o}C respectively which indicates that a higher concentration will present a higher hydrate formation temperature. As described in the literature review, the critical micelle concentration (CMC) is present at a low concentration of surfactant. In this case, where the surfactant is cationic (positive head); all the surfactant molecules may possibly adsorb onto the negatively charged barite particles, to the negatively charged xanthan gum molecules of Duotec NS or to the negatively charged carboxymethyl cellulose molecules of Polypac ELV. The surfactant molecules may rather adsorb to these surfaces than onto water molecules in the drilling fluid due to electrostatic bonds which are stronger than hydrophobic interactions. When the surfactant reaches its CMC (critical micelle concentration) the surface activity is maximized and all surfaces are covered. The rest of the surfactant molecules will undergo micellization after this point. As micelles are good nucleation sites for hydrate formation, a concentration over the surfactant´s CMC will thus cause increased hydrate formation. Micellization is also a dynamic process which may contribute to the unstable viscosity graph as well. The 6000ppm and 12000ppm concentration presented 1,2^{o}C and 0,2^{o}C of average additional subcooling to the base fluid respectively. The CMC may perhaps lie below these concentrations. At the surfactant´s CMC all the particles may be covered, and thus removal of nucleation sites and no micellization may increase the additional subcooling somewhat. The addition of these concentrations of Arquad 12-30 seems to have some, but limited inhibition power.

The addition of the anionic surfactant SDS and the addition of the amine oxide Aromox C/12-W (figure 39, 40 and 41) show slight variations in hydrate formation temperatures; 8,2^{o}C and 8,4^{o}C for 6000ppm SDS, 11,9^{o}C and 10,4^{o}C for 12000ppm SDS, and 8,4^{o}C and 8,7^{o}C for 12000ppm Aromox C/12-W. Differences in parallels are probably due to the general uncertainties. As the average hydrate formation temperatures were thus 8,3^{o}C and 11,2^{o}C for 6000ppm and 12000ppm SDS respectively, this indicates that a higher concentration of SDS will present a higher hydrate formation temperature. Aromox C/12-W (12000ppm) presented an average hydrate formation temperature of 8,6^{o}C. Both surfactants will raise the hydrate formation temperature of the base fluid, by 1,1^{o}C, 4,0^{o}C and 1,4^{o}C respectively, in contrast to the addition of the Arquad 12-30 where some additional subcooling was provided. These observations, and the negative surface charge on SDS and the non-ionic surface charge on Aromox C/12-W, may indicate that these surfactants provide more nucleation sites to the hydrate formation. The reason for this may be additional micelle formation due to their lack of ability to bind to the negatively charged surfaces of the constituents of the drilling fluid. The surfactants may bind to the barite particles due to hydrophobic interactions by their tails, but the removal of nucleation sites should have provided some extra subcooling. The surfactant should in theory also adsorb onto water molecules, distort some cage formation and thus prevent some hydrate growth which also does not seem to be the case. These surfactants only appear to create nucleation sites in the form of micelles and seem to have no inhibition power. The difference in hydrate formation temperature between the 12000ppm concentrations of the two different surfactants may be due to a difference in the ability to form micelles or in CMC´s or due to their difference in surface charge. The non-ionic surface charge on Aromox C-12/W seems to adsorb something in the drilling fluid more strongly, as less micelles seem to be formed due to the smaller raise in hydrate formation temperature (if the two 12000ppm concentrations are compared). Another mechanism may be more tightly packed surfactant molecules in one micelle-aggregate for the non-ionic surfactant molecules of Aromox C/12-W, due to repulsive forces between the anionic head groups of SDS.

Imbentin-AG/124S/040 also has a non-ionic surface charge, and the same mechanisms seem to be present as for SDS and Aromox C-12/W. Both parallels show hydrate formation of 7,0^{o}C for the 6000ppm samples, and 10,9^{o}C and 10,3^{o}C for the 12000ppm samples (figure 42 and 43). This gives an average additional subcooling of 0,2^{o}C and a raise in the hydrate formation temperature of 3,4^{o}C respectively. Differences in parallels are probably due to the general uncertainties. A higher concentration will hence raise the hydrate formation temperature. In addition, Imbentin-AG/124S/040 seems to react somewhat differently than Aromox C-12/W, although they are both non-ionic in the base fluid. At 12000ppm the hydrate formation temperature is indicated to be between the average values for SDS and Aromox C-12/W. This may be due to a difference in the ability to form micelles and/or micelle packing, or due to some kind of reaction with the base fluid due to their chemical structure. Imbentin-AG/124S/040 also seems to react more strongly with the base fluid than SDS. A non-ionic surface charge appears to work better due to adsorption than a negative one. A higher concentration of Imbentin-AG/124S/040 seems to create more nucleation sites and hence increased hydrate formation. The addition of the surfactant seems to have no inhibition power. A lower dosage than 6000ppm is probably closer to the SDS, Aromox C-12/W and Imbentin-AG/124S/040 CMC values, which may provide some inhibition effects if they react with particles in the fluid.

5.3 Base fluid with KHI and Arquad 12-30

The parallel results from the equal concentrations of Luvicap 55w and Arquad 12-30 (6000pppm/6000ppm) indicate that the KHI stabilizes the surfactant in some kind of way. Compared to the parallel results of only 6000ppm Arquad 12-30, where growth is gradual and unstable, the catastrophic growth is here clear and sudden for this combination. The parallels show hydrate formation at -3,7^{o}C and -3,0^{o}C (figure 44) and thus an average hydrate formation temperature of -3,4^{o}C. Differences in hydrate formation temperature between parallels are probably due to the general uncertainties. The additional subcooling provided by this combination is 10,6^{o}C, which is a very good result as the addition of 12000ppm Luvicap 55w gave an average additional subcooling of 5,4^{o}C. These observations indicate synergy effects between the KHI and the cationic surfactant, as 6000ppm of Luvicap 55w alone gave an average additional subcooling of 4,7^{o}C and 6000ppm of Arquad 12-30 alone gave an average additional subcooling of 1,2^{o}C. Based on the observations and on the fact that the surfactant was added prior to the KHI, a possible mechanism may be:

1. The surfactant´s cationic head group sticks to the negative barite-, xanthan gum- and carboxymethyl cellulose particles due to electrostatic bonds and thus remove nucleation sites. Electrostatic bonds are stronger than hydrophobic interactions and hence the surfactant will prefer to bind to the particles.
2. When the KHI is added, this molecule has strong affinity for water and will move into the water phase by hydrogen bonding. If particle surfaces are covered with a sufficient amount of surfactant, the KHI will not bind to these due to hydrophobic interactions. The KHI will hence serve its purpose as an inhibitor in the water phase, and the effect of the KHI will therefore be enhanced due to its higher concentration in the water phase.
3. The synergy effects may be due to the optimized effect of KHI together with the removal of nucleation sites by the surfactant. Micellization will probably occur as this was described for the 6000ppm concentration of Arquad 12-30 alone, but the inhibition effect of KHI in the water phase seems to exceed this. The dynamic process of the surfactants may be reduced as the water phase is rather occupied by KHI, and the “leftovers” of surfactant may be bound to the KHI by its hydrophobic tail due to hydrophobic interactions. This may be a reason for the more stabilized viscosity graphs. If the surfactant molecules bind to the KHI, this does not seem to affect the KHI´s alignment in the water structure and/or the former imitation properties to a great extent. If the surfactant is present in a concentration over its CMC this may be a limitation to the additional subcooling provided due to micellization. This is why other concentration ratios between Arquad 12-30 and Luvicap 55w were tested.

The KHI could also be added prior to the surfactant. The results from these parallels are shown in figure 45. The hydrate formation temperatures of the reversed addition were 0,6^{o}C and -1,2^{o}C and hence an average hydrate formation temperature of -0,3^{o}C. The average additional subcooling was thus 6,9^{o}C and the viscosity graphs show clear and sudden peaks of catastrophic growth. As the average additional subcooling of 6000ppm of Arquad 12-30 prior to 6000ppm Luvicap 55 was 10,6^{o}C, this may indicate that enhanced inhibition effect is provided by adding the surfactant prior to the KHI as discussed at the beginning of the project with chemists at M-I SWACO. Synergy effects are present, but to a less extent than when adding the surfactant first. A possible mechanism may be:

1. The KHI will mainly bind to the water phase through hydrogen bonding due to its high affinity for water, but may also adsorb to the particles through hydrophobic interactions as these bonds are of approximately the same strength. The KHI will not have its full effect in the water phase.
2. When the surfactant is added, the particles will be partly covered with KHI. This means less adsorption surfaces for the surfactant, a larger degree of micellization and hence more nucleation sites in the fluid. Surfactant may bind to the water phase due to hydrophobic interactions, but as shown for samples of Arquad 12-30 only, the surfactant alone seems to have approximately no inhibition power.
3. Decreased effect of the KHI and increased micellization is a possible reason for the decline in average additional subcooling for the same concentration ratio between the KHI and the surfactant added in the opposite order.

As the 6000ppm/6000ppm concentration ratio with the surfactant added prior to the KHI combination presented excellent results, tests were performed on other concentration combinations to look for possible enhanced synergy effects. For example a lower concentration of Arquad 12-30 should in theory reduce some micellization, as this may be closer to the surfactant´s CMC. This would reduce nucleation sites and hence the hydrate formation. The parallel results of 9000ppm Luvicap 55w and 3000ppm Arquad 12-30 presented hydrate formation temperatures of 2,8^{o}C and 0,5^{o}C (figure 46) and thus an average hydrate formation temperature of 1,7^{o}C. The average additional subcooling provided by this combination was hence 5,5^{o}C. The viscosity graphs show a somewhat more gradual increase than for the 6000ppm/6000ppm ratio which indicates somewhat more instability in the sample. These observations show that there may be some degree of synergy effects present as the average additional subcooling is similar to that of 12000ppm of Luvicap 55w alone (5,4^{o}C). The mechanism, as described for the 6000ppm/6000ppm ratio probably occur, but to a lower degree. The concentration of surfactant is probably too low to cover all the particles in the sample and hence the lower degree of subcooling provided. The more gradual growth and the variations in hydrate formation temperatures may thus be caused by the KHI randomly binding with the particles and the water phase in the fluid.

The opposite concentration ratio (3000ppm Luvicap 55w and 9000ppm Arquad 12-30) presented more unstable viscosity graphs before catastrophic growth was reached. This may be due to the high concentration of surfactant which may cause the same dynamic micellization as for the surfactant alone. This relationship gave hydrate formation temperatures of -0,5^{o}C and 0,1^{o}C (figure 47) and thus an average hydrate formation temperature of -0,2^{o}C. The average additional subcooling was hence 7,4^{o}C which is less than for the 6000ppm/6000ppm ratio, but shows a higher degree of synergy effects and higher average additional subcooling than for the opposite combination. This indicates that a high concentration of the cationic surfactant is much more crucial than a high concentration of Luvicap 55w (in combination). This may point toward that the covering of particles is the more important function, so that the KHI can work in the water phase. The observations show that the KHI concentration still needs to be higher to provide a higher degree of subcooling in the fluid as the results were better for the 6000pppm/6000ppm ratio. In addition, the concentration of surfactant needs to be reduced as there may be too many micelles/nucleation sites due to a concentration far over its CMC. An optimal concentration ratio needs to be found between the two substances.

As the results indicated that the concentration of Arquad 12-30 needed to be higher than 3000ppm and lower than 9000ppm, another combination was tested. The selected concentration ratios were 7000ppm Luvicap 55w and 5000ppm Arquad 12-30 and the opposite ratio, 5000ppm/7000ppm. The parallel results showed hydrate formation temperatures of 1,5^{o}C and 0,5^{o}C, and 1,6^{o}C and -1,5^{o}C respectively, and hence average hydrate formation temperatures of 1,0^{o}C and 0,1^{o}C (figure 48 and 49). The viscosity graph of the 7000ppm/5000ppm ratio seems to be somewhat more unstable compared to the opposite ratio. The viscosity graph of the 5000ppm/7000ppm ratio presents clear and sudden catastrophic hydrate growth similar to the 6000ppm/6000ppm ratio. This is opposite than for the 9000ppm/3000ppm and 3000ppm/9000ppm where the ratio with the higher concentration of the surfactant was the more unstable. This may indicate that the concentration of surfactant has to lie nearby this ratio (5000ppm/7000ppm) for optimized effect. The additional subcoolings provided by the 7000ppm/5000ppm relationship and the opposite were 6,2°C and 7,1°C respectively. These results show that the concentration of Arquad 12-30 needs to be higher than 5000ppm as the additional subcooling is higher when added at 6000ppm in combination with the KHI (10,6°C). The results also indicate that a lower concentration than 7000ppm of surfactant needs to be added in combination with KHI. The results point to that the surfactant concentration is the critical factor and not the concentration of KHI, as a higher concentration of surfactant provides a higher degree of additional subcooling.

The 6000ppm/6000ppm combination of Luvicap 55w and Arquad 12-30 seems to present the optimal concentration combination between the two, and provide the highest degree of additional subcooling of the selected combinations. Other combinations around the 6000ppm/6000ppm ratio may contribute to even more additional subcooling. A key to this good result may also be the 1:1 ratio, where the concentration may be reduced to possibly produce as favorable results. This requires further testing.

5.4 Base fluid with KHI and SDS or Aromox C-12/W or Imbentin-AG/124S/040

The viscosity graphs obtained from the tests with KHI added together with SDS or Aromox C-12/W or Imbentin-AG/124S/040 also show a higher degree of stability than those obtained by the surfactants alone, when added at the same concentrations (6000ppm/6000ppm). The charge of the surfactants does not seem to affect this stabilization. This may be due to the reduced dynamics of the surfactants as the KHI is occupying the water phase, or that the "leftover" surfactant molecules bind to the KHI´s hydrophobic parts by hydrophobic interactions. The anionic surfactant SDS show more unstable parallel results of the hydrate formation temperatures; 4,0°C and 1,5°C (figure 51) and thus an average of 2,8°C. The non-ionic surfactants Aromox C/12-W and Imbentin-AG/124S/040 show more stable parallel results; 2,9°C and 3,5°C and thus an average of 3,2°C, and 4,8°C and 4,2°C (figure 52 and 53) and thus an average of 4,5°C respectively. Differences in parallels are probably due to the general uncertainties. A reason for the more unstable results for SDS may be the due to the surfactant´s surface charge compared to the non-ionic ones. The average additional subcoolings for these combinations were 4,4°C (SDS), 4,0°C (Aromox C-12/W) and 2,7°C (Imbentin-AG/124S/040), hence the SDS seems to work the best of the three. This may be due less binding of the anionic SDS to the KHI or some other unknown mechanism. If a substance binds to the KHI this may reduce its effect. The KHI may not be able to align into ice crystal structure or imitate a former. The non-ionic surfactants may be able to bind more strongly to the KHI. In theory these three substances will not bind to the particles in the fluid due to electrostatic interactions due to their surface charges. This is shown for the samples with only the surfactants present, where hydrate formation temperatures were raised. The surfactants may enter and leave the water phase until the KHI is added. Aromox C-12/W which raised the temperature the least alone, has the best effect of the two non-ionic surfactants in combination with KHI. This may be due to a difference in micelle formation/packing as described for the surfactants added alone. SDS should have larger (more) micelles due to the negative and thus repulsive surface charge, but still it indicates that this surfactant works better. As the average additional subcooling of only 6000ppm Luvicap 55 alone was 4,7^{o}C, there seems to be no synergy effects present together with SDS (6000ppm/6000ppm) as this is approximately the same value. Aromox C-12/W and Imbentin-AG/124S/040 are indicated to be antagonistic in combination with KHI (6000ppm/6000ppm) as their average additional subcoolings are decreased compared to the samples with only 6000ppm of the KHI.

5.5 Base fluid with KHI and AA´s

The two special designed AA´s (Cdld-151 and Cdld-445) were selected due to their structures being analogous to Arquad 12-30, which showed the best performance. These surfactants have typical anti-agglomerant structures and are cationic, but were used as surfactants in this study. The viscosity graphs show gradual and very unstable hydrate growth (figure 54). Only one test was performed on each sample in the combination with Luvicap 55w (6000ppm/6000ppm) due to time constraints, and also on the fact that they presented exactly the same hydrate formation temperatures (5,7^{o}C). These combinations hence provided an average additional subcooling of 1,5^{o}C to the base fluid. This may indicate antagonism between the KHI and the AA´s as the average average additional subcooling of 6000ppm of only Luvicap 55 was 4,7^{o}C. As the 6000ppm/6000ppm relationship between Luvicap 55w and Arquad 12-30 presented an average additional subooling of 10,6^{o}C, the poor results with the AA´s may be due to a difference in the cationic surfactans´ structures. Typical AA structures have tri-butyl groups bound to their head parts, while Arquad 12-30 has tri-methyl groups bound to the head part. This indicates that a smaller cationic head group on the surfactant enhances performance drastically. The AA´s instability and also the reduced subcooling contribution may be a result of a larger amount of micelles as fewer molecules may aggregate in one micelle. Less AA molecules may fit around the particles and hence enhanced micellization could be the result. This is the poorest result of all the combinations, which may be a result of that the AA´s contain the largest head groups of all the surfactants tested. They are also heavier which means they could bind to the KHI and hence reduce the effect by hindering the KHI from fitting into the ice crystal structure or being able to imitate a former. Similar structures with the same size as Arquad 12-30 may be other possible synergists, or structures with longer or shorter carbon chains due to surface activity. This needs to be evaluated.

SDS, Aromox C-12/W, Imbentin-AG/124S/040 and the anti-agglomerants may give better results if tested at other ratios. This needs to be evaluated.

5.6 WBM compatibility of additives

Rheology measurements, pH-measurements and API fluid loss did not generally present any major differences compared to the base fluid when Luvicap 55w (12000ppm) or Luvicap 55w with the different surfactants/anti-agglomerants (6000ppm/6000ppm) were added. The small differences can easily be adjusted back to the original parameters. The small differences may be a result of a few uncertainties when performing the tests, like when two different viscometers were used this may have provided slightly different results. Another uncertainty is when performing rheology measurements at cold temperatures ($2^{o}C$). The cooling bath is not 100% stable and will provide somewhat varying temperatures. The small differences may also be due to various chemical reactions between the base fluid and the additives.

5.7 An evaluation of the best combination

The best combination obtained from this study was clearly the combination of 6000ppm Arquad 12-30 added prior to 6000ppm of Luvicap 55w, as this combination provided an average additional subcooling of $10{,}6^{o}C$ to the base fluid. Compared to the average additional subcooling provided by 12000ppm of Luvicap 55w ($5{,}4^{o}C$) this is almost double the effect, which is a very good result. By using this combination in Glydril 1,1SG the amount of THI´s may be reduced considerably and the fluid could be used for deepwater drilling. By adding the surfactant the KHI may exceed its limited subcooling properties. This combination may have limitations in other fluid systems due to different constituents, and may also have limitations for other than exclusively gas systems. This needs to be evaluated.

Arquad 12-30 is commercially available which is favorable. Arquad 12-30 generated a moderate amount of foam, but this can be removed by the use of defoamer. According to the safety-datasheets of Arquad 12-30 this substance is very toxic for aquatic organisms like fish, invertebrates and algae. Personal protective equipment is required. On the other hand there are no dangerous degradation products and no unfavorable breakdown products if used as advised. The substance contains easily biodegradable substances. Arquad 12-30 is classified as a red chemical according to the HOCNF, and may therefore not be used as an oil-field chemical in WBM. Alternative analogues therefore need to be investigated.

6 CONCLUSION

Hydrate growth in the base fluid with Luvicap 55w seems to be clear and sudden and at a specific temperature. Hydrate growth in samples with only the surfactants appear to be gradual and random. This phenomenon seems to be independent of surface charge and concentration. A higher concentration of surfactant generally tends to increase the hydrate formation temperature, which points to that the CMC is an important factor in creating nucleation sites. The only surfactant that provides additional subcooling to the base fluid on its own is Arquad 12-30 (when added at 6000ppm, 1,2°C). The other surfactants raise the hydrate formation temperatures of the base fluid when added alone.

When the surfactants is added together with Luvicap 55w, the KHI generally seems to stabilize the surfactant, and hence the hydrate growth becomes more sudden and at a specific temperature. The AA´s do not seem to be stabilized in the same matter with Luvicap 55w. The 6000ppm/6000ppm ratio of Luvicap 55w in combination with Arquad 12-30, SDS, Aromox C-12/W, Imbentin-AG/124S/040 indicate average additional subcoolings of 10,6°C, 4,4°C, 4,0°C and 2,7°C respectively. The AA´s (Cdld-151 and Cdld-445) point to an average additional subcooling of 1,5°C. In comparison to the 6000ppm addition of only Luvicap 55w, this indicates antagony effects or no effects at all for all additives except from Arquad 12-30. Test results from adding the KHI prior to Arquad 12-30 in the 6000ppm/6000ppm ratio, indicate an average additional subcooling of 6,9°C, which is a poorer result than the opposite order of addition. The addition of surfactant prior to the KHI seems to give better effect. Other ratios of Luvicap 55w and Arquad 12-30 tested (9000ppm/3000ppm, 3000ppm/9000ppm, 7000ppm/5000ppm and 5000ppm/7000ppm) point to average additional subcoolings of 5,5°C, 7,4°C, 6,2°C and 7,1°C respectively, which is poorer results than for the 6000ppm/6000ppm ratio. These results indicate that the concentration of surfactant (particle coating) is a more critical factor than the concentration of the KHI.

A cationic surfactant with a smaller head group such as Arquad 12-30, seems to provide the most additional subcooling due to its positive surface charge. Arquad 12-30 contains tri-methyl groups while the AA´s contains tri-butyl groups, and the AA´s presented much poorer results in providing additional subcooling due to its cationic nature. It is thought that this surfactant works in coating negative particles in the fluid, and hence enhanced effect of the KHI in the water-phase is a possible result. The synergy effects from this combination appear to provide double effect compared to that of 12000ppm of Luvicap 55w.

Standard WBM tests showed that these additives did not induce any major differences in properties that cannot easily be adjusted back to the original parameters/properties.

The excellent result of 6000ppm/6000ppm of Luvicap 55w and Arquad 12-30 could potentially reduce the use of THI significantly in DW WBM for use in deepwater drilling.
Further testing is recommended, as described in the recommendations chapter.

7 RECOMMENDATIONS

- Confirm the results in this study by performing more test-parallels. Check the validity of the results by performing statistical tests (e.g. a T-test).
- Test for hydrate formation temperatures around the 6000ppm/6000ppm ratio of Luvicap 55w in combination with Arquad 12-30 to see if this could provide even more additional subcooling as a higher degree of synergy may be present.
- A key may be the 1:1 ratio, so tests should be performed with lower concentrations to investigate if this provides as favorable effects as for the 6000ppm/6000ppm ratio of Luvicap 55w and Arquad 12-30.
- Test other concentration ratios for the other surfactants/anti-agglomerants in this study, as a possible higher degree of synergy may appear from this.
- Other analogues to Arquad 12-30 should be tested as this chemical is classified as red according to the HOCNF. This head-group size seems to work the best, and in-house synthesis of analogues is a possibility. Analogues with different carbon chain-lengths could also be tested as this presents a difference in surface activity.
- Adsorption studies may be performed to evaluate if the assumed mechanisms in this study are correct.
- The combinations can be evaluated on their induction times.
- Tests must be performed to see if the synergy effects of Luvicap 55w and Arquad 12-30 last/are stable over time in the drilling fluid.
- Evaluate the combination of Luvicap 55w and Arquad 12-30 in other fluid systems.

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9 LIST OF APPENDIX

APPENDIX A: Glydril Mixing - Procedure

(SWACO, 2011a).

3.2 Inhibitive / Polymer water based fluids - rev 0, 20.Feb.2011

GENERAL

This procedure is applicable for the following drilling fluid systems: **GLYDRIL, GLYDRIL DW, KCL / POLYMER, SILDRIL**

EQUIPMENT

Hamilton Beach mixer / Silverson mixer
Electronic balance
pH meter
Mixing container, weighting boats, 10 ml syringe, spatel

ORDER OF ADDITION

The order of mixing is given in table below. If some of the products are not included in the formulation, please skip these steps.

Order of addition	Mix time - minutes
Prehydrated Bentonite (PHB)	0
Fresh Water	1
Salts	2
pH additive to treat out any hardness	2
Viscosifier	10
Fluid loss control additives	10
Other liquid additives	5
Weighting agent	20
pH additive to specified pH -range	2

PROCEDURE

- For large volumes mix 1000 ml or 1400 ml on a Silverson mixer. For small volumes mix 350 ml or 500 ml on a Hamilton Beach mixer.
- Add prehydrated bentonite (if required) followed by water to a mixing container. Mix for 1 minute at a speed adequate to maintain a vortex. If PHB is not included, just add water to the mixing container.
- Add salt and mix for 2 minutes.
- Add pH additive to treat out any hardness, and mix for 2 minutes.
- Add viscosifier slowly into the vortex, ensuring that all polymers have completely dispersed and that nothing adheres to the side of the mixing container or the mixing head. Total mixing time = 10 minutes.
- Add the fluid loss additives slowly into the vortex, ensuring that all polymers have completely dispersed and that nothing adheres to the side of the mixing container or the mixing head. Total mixing time = 10 minutes.
- Add other liquid additives and mix for 5 minutes.
- Add weighting agent during a 5 minutes period and mix for further 20 minutes.
- Add pH additive to adjust to specified pH-range and mix for 2 minutes.

Note: Ensure temperature of the fluid does not exceed 60°C during the mixing process. If the fluid reaches 60°C, place the mixing cup in a water bath during further mixing to cool it down.

STANDARD PRODUCTS - INHIBITIVE / POLYMER WATER BASED FLUIDS

Examples of typical products for the different inhibitive / polymer water based fluids are given in the table below

Products	Glydril	Glydril DW	KCl/Polymer	Sildril
Prehydrated Bentonite			(PHB)	(PHB)
Fresh Water	FW	FW	FW / SW	FW
Salts	KCl	NaCl / KCl	KCl	NaCl / KCl
PH additive to treat out any hardness	Soda Ash Pot. Carb. Lime NaOH KOH	Soda Ash Pot. Carb. Lime NaOH KOH	Soda Ash Lime NaOH KOH	Soda Ash Lime NaOH KOH
Viscosifier	Duovis, Duotec NS, Flowzan, Duovis Plus NS, Celpol R, CMC HV			
Fluid loss control additives	Flotrol, Trol FL, Polypac ELV, Polypac UL, CMC LV/HV			
Hydrate Inhibition		MEG		
Scale Inhibitition	Glydril MC	Glydril MC		Sildril L
Weighting agent	Barite $CaCO_3$	Barite $CaCO_3$	Barite $CaCO_3$	Barite $CaCO_3$

Products	Glydril	Glydril DW	KCl/Polymer	Sildril
pH additive to adjust to specified range	pH = 8-8.5	pH = 8-8.5	pH = 9-9.5	pH = 11-12*

***) The pH is depending on the silicate concentration in the formulation.**

APPENDIX B: pH-Measurement - Procedure
(SWACO, 2011a).

5.1 PH - rev 0, 20.Feb.2011

Standard pH range in water based drilling fluids is pH 9-12. Many of the additives have an optimum pH range for maximum performance (yield, solubility), but higher pH also reduces corrosion of steel and reduces bacteria growth.

EQUIPMENT

- Electronic glass-electrode pH meter
- Buffer solutions (pH 4.0, 7.0 and / or 10.0 - as applicable)
- Deionised water

CALIBRATION

1. Calibrate pH meter using appropriate buffer solutions.
2. Rinse probe using deionised water.
3. Store probe in 3M KCl solution.

PROCEDURE

1. Rinse electrode with deionised water.
2. Place electrode in sample to be tested and stir gently. Allow time for the reading to stabilize.
3. Report sample pH to nearest 0.1 pH unit.
4. Clean electrode and store in a vial or beaker with 3M KCl solution.

Note: pH measurements of formates or WBM's containing formates requires a 1:10 dilution.

For additional information, see API Recommended Practice 13B-1, section 9.

APPENDIX C: Calibration of Fann 35 - Procedure
(SWACO, 2011a).

MI SWACO

HANDBOOK FOR CONTROL AND CALIBRATION OF LABORATORY EQUIPMENT

Procedure - Calibration of FANN 35 VISCOMETER

Procedure:

1. Check FANN 35 VISCOMETER with OFITE solution once a week, before use or when necessary.
2. Acceptable deviance ± 1.5 units.
3. Register data in **Calibration Manager** according to procedure 1 in control and calibration of laboratory equipment.
4. Procedure will be performed by user.

Control:

Equipment: OFITE Calibration solution 100 cP, thermocup, reference thermometer.

<u>The reference thermometer will be certified once a year by an authorized approved extern firm.</u>

1. Clean bob and sleeve.
2. Fill OFITE calibration solution in thermocup.
3. Place the thermocup on the VG-meter stand. Pull the stand up, thermocup is in the correct position when solution hits the mark on sleeve.
4. Turn the VG-meter on 600rpm and let it run for 5-10 minutes. All components in contact with solution and the fluid itself need to achieve the same temperature.
5. When temperature is stabile, make a note of the values at 600 rpm and 300 rpm.
6. Control the given temperature up against calibration form received with the OFITE calibration solution. Write down cP designated on form to the specific temperature measured.

7. Calculation of given values:
   600 rpm noted x 0,505 = value
   300 rpm noted x 1 = value

8. Control values against cP value from step 6. Acceptable deviance is ± 1.5 units.
9. Register values and other useful data in **Calibration Manager** according to procedure 1.

Note: If device is out of spec, perform control steps 1-9 again. Be sure that OFITE calibration solution and followed cP form shows the same batch number. Calibration has to be performed if VG-meter shows a deviance over ± 1.5 units (view procedure below).

Approved by:

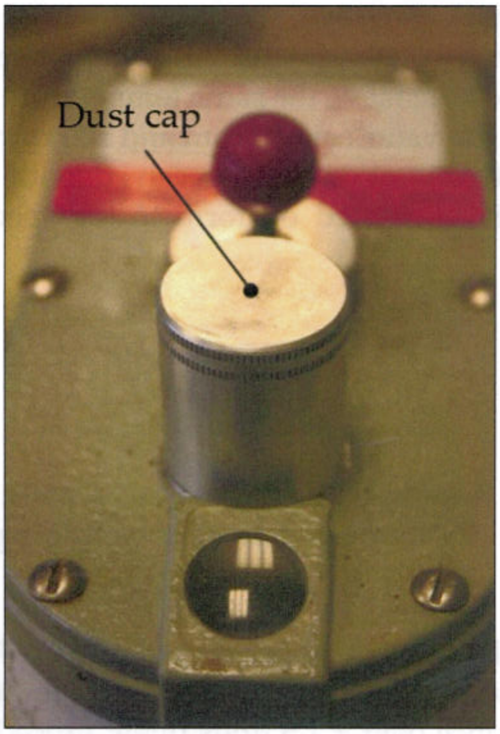
Procedure - Calibration of FANN 35 VISCOMETER

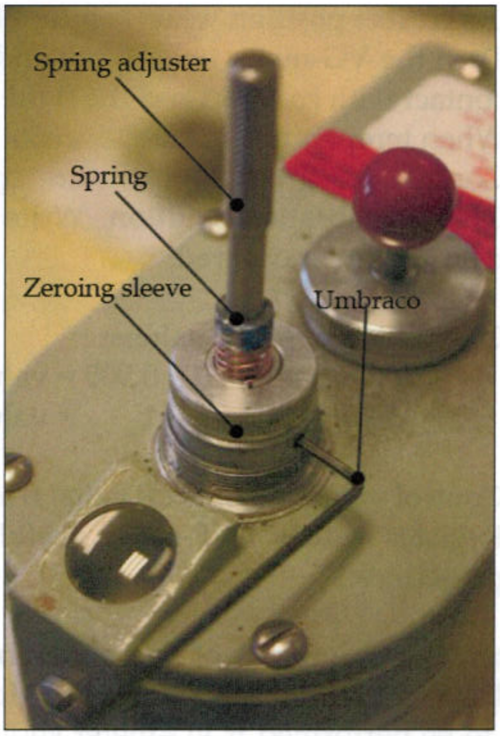
Calibration:

Equipment: Umbraco key, spring adjuster.

Always be sure that value is at zero before performing all steps of the calibration procedure, if not, only perform step 1-3 and do another control.

1. Unscrew "dust cap" on VG-meter.
2. Spring can be seen.
3. Hold spring with two fingers and place umbraco key in the zeroing sleeve, open the screw so the spring is loose with possibilities to turn left, right, up and down (here you can adjust and "zero out" the values of VG-meter).
4. Place "spring adjuster" in the middle of spring.
5. Turn "spring adjuster" to the left for higher value, and to the right for lower value. Start off with turning only 1/8 of a round.





Note: There are small adjustments required to calibrate device.

Approved by:

6. Adjust and "zero out" the values of VG-meter by turning spring left/right/up and down with fingers, close the "zeroing sleeve" with umbraco key while value is at zero and spring is correctly placed in the zeroing sleeve.
7. Perform another control procedure with solution, step 1-8.
8. Register values and other useful data in **Calibration Manager** according to procedure 1.
9. If device is still out of spec, perform calibration steps again.

Note: If device is not within range of calibration, service will have to be performed. Contact an authorized dealer or communicate with individual responsible for maintenance and calibration of equipment.

APPENDIX D: Rheology, Fann 35 - Procedure
(SWACO, 2011a).

4.2.2 Fann 35 - rev 0, 20.Feb.2011

EQUIPMENT

VG-meter (model FANN 35)
Thermo-cup
Thermometer/ Temperature regulator

Fig. 4.6 Fann 35

PROCEDURE

1. Place a sample of mud in the thermo-cup. Immerse the rotor into the mud exactly to the scribed line.
2. Set the rotation speed to 600 rpm and heat the mud to the desired temperature and a steady reading are obtained, record this reading.
3. While rotation, shift to 300 rpm and wait until the reading is steady prior to recording it.
4. Record the readings at 200, 100, 6 and 3 rpm
5. Shift to 600 rpm once more and stir the mud for 10 seconds.
6. Allow the mud to stand undisturbed for 10 seconds then turn the instrument on 3 rpm and record the maximum reading. This reading represents the 10 seconds GEL strength in lbs/100 sq ft.(The reading divided by 2 represents the 10 seconds GEL strength in Pa).
7. Re-stir the mud at 600 rpm for 10 seconds then allow the mud to stand undisturbed for 10 minutes prior to repeating the test at 3 rpm. This reading represents the 10 minutes GEL strength in lbs/100 sq ft(The reading divided by 2 represents the 10 minutes GEL strength in Pa).

The PLASTIC VISCOSITY, PV, in centipoise equals the 600 rpm reading (step 2 above) minus the 300 rpm dial reading (step 3 above).

The YIELD POINT, YP, in lbs/100ft^2 equals the 300 rpm dial reading (step 3 above) minus the Plastic Viscosity.
(The YIELD POINT, YP, in Pa is YP in lbs/100ft^2 divided by 2).

Caution: Stop the VG-meter before cleaning the rotor. Wear heat-resistant gloves when cleaning hot thermo-cup.

For additional information, see API Recommended Practice 13B-1, section 4.3 for water based mud and API Recommended Practice 13B-2, section 4.3 for oil based mud.

APPENDIX E: Hot Rolling - Procedure

(SWACO, 2011a).

4.3.1 Hot-rolling and Static ageing - rev 0, 20.Feb.2011

EQUIPMENT:

Heating oven, roller oven, ageing cell

Fig. 4.19 Ageing cell

SAMPLE:

Recommended volume is 350 ml fluid per cell. If more fluid is needed, remember that the fluid will need some space for expanding when heated. At temperatures above 150°C a volume of 350 ml is the maximum.

NOTE: At temperatures above 120°C, WBM mud requires a few drops of oxygen scavenger to protect the polymers from "burning". The following oxygen scavengers are recommended dependent on base fluid:

Brines	Oxygen scavenger
Monovalent brines; i.e. Sodium, Potassium	**Safe-Scav NA** (Ammonium bisulfite)
Divalent brines; i.e. Calcium, Zink also Chloride/Bromine	**Safe-Scav CA**
Formate brines	**Safe-Scav CA**

PROCEDURE FOR HOT-ROLLING/DYNAMIC AGEING:

- Ensure that all assembling parts of the ageing cell are marked with the same reference number and that the stem valve and lid is not blocked.
- Transfer approximately 350 ml of fluid to an ageing cell (a small metal device made especially for the cell, showing the correct level, may be used).
- Close the cell by the two lid-parts, with a metal-ring placed between them and tighten the screws. Insert the stem valve, if not already in place, and leave it slightly open.
- Pressurise the cell through the stem valve with nitrogen (inert gas). Consult the table of pressure required vs. vapour pressure of the fluid phase and ageing temperature for the drilling fluid, Table 1. This is done to prevent the fluid from boiling (both OBM and WBM) and to remove oxygen to prevent bacterial growth and/or "burning" of the polymers (WBM). Check for leakage, applying water on top of the lid and the valve and look for air bubbles.
- Preheat the roller oven to the desired temperature, and place the cell horizontally onto the rollers. Standard hot-rolling time is 16 hours, or hot-roll for the required time.
- **Use dry heat resistant gloves when taking the cell out of the oven.** Cool down the cell, and **carefully bleed off the pressure. This should be done in a ventilated area or in a fume cupboard.**

PROCEDURE FOR STATIC AGEING:

Follow the same procedure as for hot-rolling, but place the cell in a vertical position without rolling.

Suggested Applied pressure at various ageing temperatures.

Ageing Temperature,°C	Water Vapour Pressure, psi	Suggested Applied Pressure, psi
100	14,7	25
121	30	50
149	67	100
177	135	150
205	247	250

APPENDIX F: API Fluid Loss - Procedure (SWACO, 2011a).

4.4.1 API Fluid Loss Test - rev 1, 27.Dec.2011

EQUIPMENT:

API Filterpress, 90-millimeter Whatman Filterpaper No.50 or equivalent, timer, graduated cylinder

Fig. 4.21 API Static Filterpress

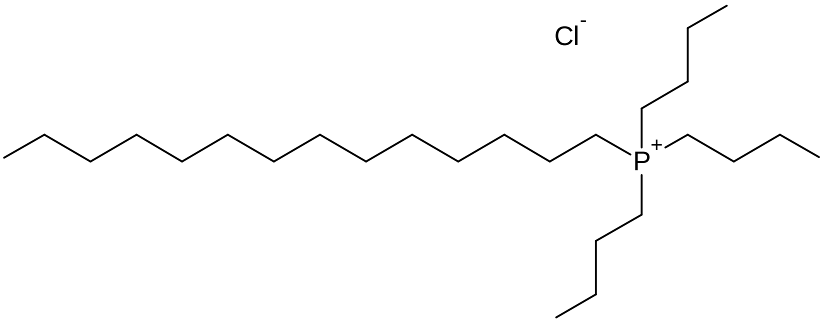
PROCEDURE:

- Make sure that all parts of the standard API filter press are clean, dry and that nothing is plugging the outlet in the bottom part.
- Place the bottom part in a stand with the outlet facing downwards.
- Insert a sealing ring into the groove, and then the screen/sieve followed by a filter and a second sealing ring on the top.
- Screw the body cell into the bottom part ensuring that they are properly mounted and sealed; this to avoid leakages.
- Fill the cell with fluid, saving 1-1,5 cm to the top and mount it into the support frame with a clean lid and sealing. Turn the locking screw downwards into the centred groove in the lid and seal the assembly properly.
- Place a dry graduated cylinder under the drain tube to collect the filtrate. Close the pressure relief valve and apply pressure by adjusting the regulator to give a pressure of 100 (+/-5)psi.
- Start the timer when the pressure is first applied. The total filtrate volume is measured after 30 minutes. NB! Maintain the pressure at 100 psi during the test.
- If spurt volume is needed, this is generally taken within the first 30 sec.
- Shut off the pressure regulator after 30 minutes and carefully open the pressure relief valve. Disassemble the cell after all pressure is released. Pour out the fluid and examine the filter cake.

- Report the filter cake thickness in mm and the API fluid loss in ml to the closest 0,1ml. Also note the filtercake's texture as; hard, soft, rubbery, firm, etc.
- **For additional information, see API Recommended Practice 13B-1, section 7.2.**

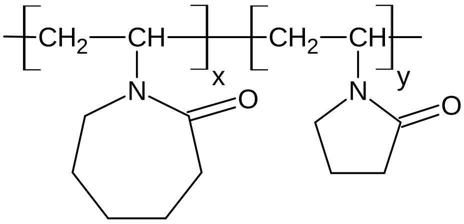
APPENDIX G: Chemical structures of surfactants, anti-agglomerants and some relevant drilling fluid additives

AA General Structure



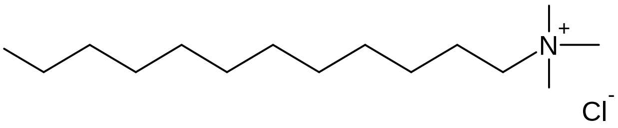
(Tri-n-butyl)-n-tetradecylphosphonium chloride

Luvicap 55w



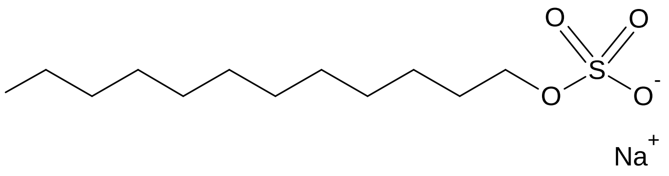
1:1 vinyl caprolactam:vinyl pyrrolidone copolymer.

Arquad 12-30



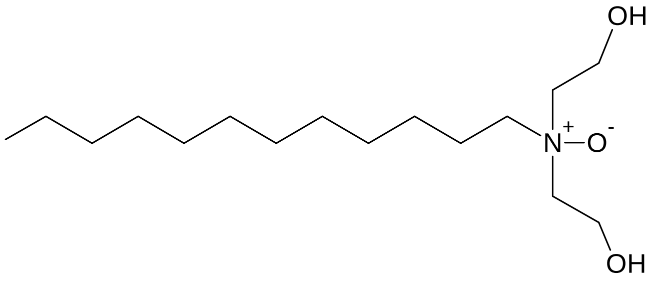
Dodecyltrimethylammonium chloride

SDS



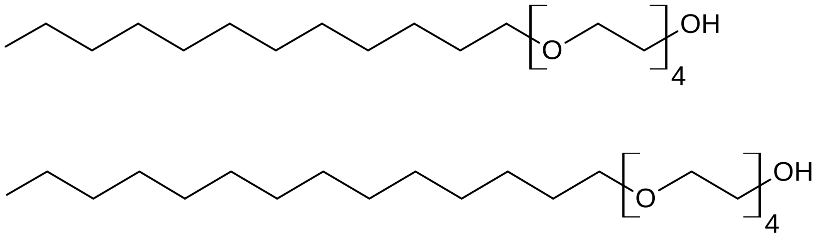
Sodium Dodecyl Sulfate

Aromox c/12-w



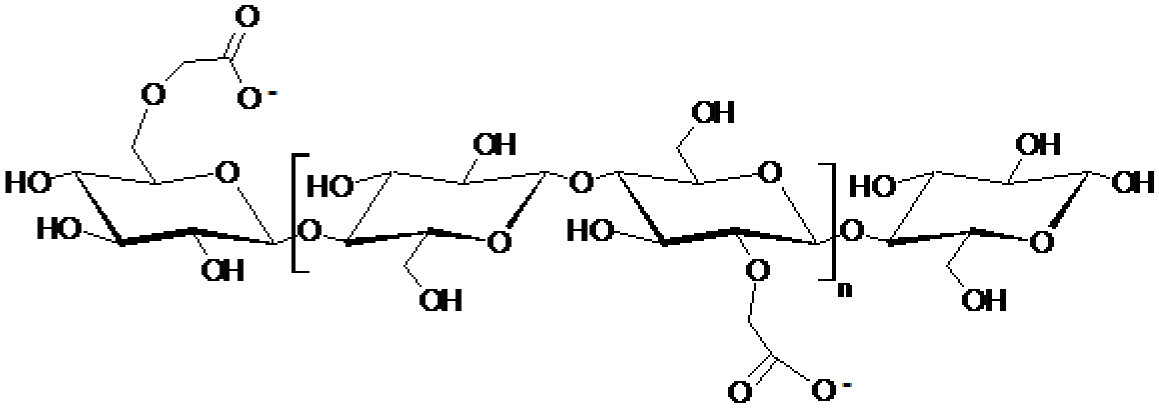
Bis(2-Hydroxyethyl) Cocoamine Oxide

Imbentin-AG/124S/040



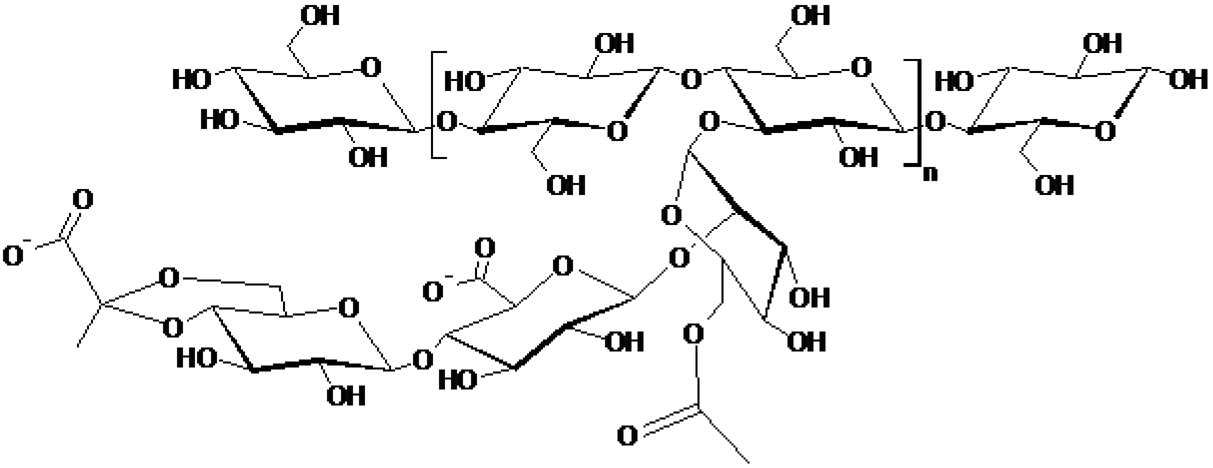
Alcohol C12-14 + 4 EO

Polypac ELV



Carboxymethyl cellulose

Duotec NS



Xanthan gum

APPENDIX H: Safety-datasheets for chemicals used in this study.

Safety data sheet

BASF Safety data sheet according to 91/155/EEC
Date / Revised: 23.08.2005 Version: 2.0
Product: **Luvicap* 55 W**

(30243840/SDS_GEN_EU/EN)

Date of print 04.10.2010

1. Substance/preparation and company identification

Luvicap* 55 W

Use: Performance Chemicals for Oilfield Applications

Company:
BASF SE
67056 Ludwigshafen
GERMANY
Global Oilfield Soilutions
Telephone: +49 621 60-52555
Telefax number: +49 621 60-41517
E-mail address: product-safety-oilfield-applications@basf.com

Emergency information:
International emergency number:
Telephone: +49 180 2273-112

2. Composition/information on ingredients

Chemical nature

Polymer based on: 1-vinyl-2-pyrrolidone, vinylcaprolactam, in water

3. Hazard identification

No particular hazards known.

If the product adheres to skin, irritation may occur when it dries.

4. First-aid measures

General advice:
Remove contaminated clothing.

If inhaled:
Keep patient calm, remove to fresh air, seek medical attention.

On skin contact:
Wash thoroughly with soap and water.

On contact with eyes:
Immediately wash affected eyes for at least 15 minutes under running water with eyelids held open, consult an eye specialist.

On ingestion:
Rinse mouth immediately and then drink plenty of water, seek medical attention.

5. Fire-fighting measures

Suitable extinguishing media:
water spray, dry extinguishing media, foam, carbon dioxide

6. Accidental release measures

Methods for cleaning up or taking up:
For small amounts: Pick up with absorbent material (e.g. sand, sawdust, general-purpose binder).
Dispose of absorbed material in accordance with regulations.
For large amounts: Pump off product.
For residues: Rinse away with water.

7. Handling and storage

Handling

Handle in accordance with good industrial hygiene and safety practice. Keep container tightly sealed.

Protection against fire and explosion:
No special precautions necessary.

Storage

Further information on storage conditions: Store protected against freezing.

8. Exposure controls and personal protection

Personal protective equipment

Hand protection:
Suitable chemical resistant safety gloves (EN 374) also with prolonged, direct contact (Recommended: Protective index 6, corresponding > 480 minutes of permeation time according to EN 374): E.g. nitrile rubber (0.4 mm), chloroprene rubber (0.5 mm), polyvinylchloride (0.7 mm) and other
Supplementary note: The specifications are based on own tests, literature data and information of glove manufacturers or are derived from similar substances by analogy. Due to many conditions (e.g. temperature) it must be considered, that the practical usage of a chemical-protective glove in practice may be much shorter than the permeation time determined in accordance with EN 374.

Eye protection:
Safety glasses with side-shields (frame goggles) (EN 166)

9. Physical and chemical properties

Form:	liquid	
Colour:	colourless, clear	
Odour:	faint odour	
pH value:	approx. 8 (approx. 100 g/l, 23 °C)	(DIN/ISO 976)
Boiling point:	approx. 100 °C (1.013 mbar)	
Vapour pressure:	approx. 20 mbar (20 °C)	
Density:	approx. 1.11 g/cm3 (20 °C)	(ISO 2811-1)
Solubility in water:	soluble 150 g/l	
Miscibility with water:	completely (e.g. >=90%)	
Viscosity, dynamic:	100 - 1,800 mPa.s (23 °C)	
Solids content:	approx. 50 %	

10. Stability and reactivity

Thermal decomposition: No decomposition if used correctly.

Hazardous reactions:
No hazardous reactions when stored and handled according to instructions.

11. Toxicological information

LD50/oral/rat: > 2,000 mg/kg

Primary skin irritation: non-irritant

Primary irritations of the mucous membrane: non-irritant

If the product adheres to skin, irritation may occur when it dries.

Additional information:

The statement was derived from products of similar composition.

12. Ecological information

Ecotoxicity

Toxicity to fish:
OECD Guide-line 203 static
Brachydanio rerio/LC50 (96 h): 10,000 mg/l

Aquatic invertebrates:
OECD Guideline 202, part 1 static
Daphnia magna/EC50 (48 h): > 100 mg/l

Microorganisms/Effect on activated sludge:
OECD Guideline 209 aerobic
activated sludge/EC20 (0.5 h): 1,000 mg/l

Assessment of aquatic toxicity:
There is a high probability that the product is not acutely harmful to aquatic organisms.
The inhibition of the degradation activity of activated sludge is not anticipated when introduced to biological treatment plants in appropriate low concentrations.

Persistence and degradability

Elimination information

Method of analysis:	DOC reduction
Degree of elimination:	0 - 10 %
Evaluation:	Poorly biodegradable.

Additional information

Other ecotoxicological advice:
Ecological data are determined by analogy.

13. Disposal considerations

Must be dumped or incinerated in accordance with local regulations.
A waste code in accordance with the European waste catalog (EWC) cannot be specified, due to dependence on the usage.
Observe national and local legal requirements.

14. Transport information

Not classified as hazardous under transport regulations (ADR RID ADNR IMDG/GGVSee ICAO/IATA)

15. Regulatory information

Regulations of the European union (Labelling) / National legislation/Regulations

Directive 1999/45/EC ('Preparation Directive'):

The product does not require a hazard warning label in accordance with EC Directives.

Classification and labelling were undertaken on the basis of tests on a preparation of similar composition.

Other regulations

The information fulfills the requirements of Directive 1999/45/EC concerning preparations and the associated requirements for 'safety data sheets'.

16. Other information

Any other intended applications should be discussed with the manufacturer.

Vertical lines in the left hand margin indicate an amendment from the previous version.

The data contained in this safety data sheet are based on our current knowledge and experience and describe the product only with regard to safety requirements. The data do not describe the product's properties (product specification). Neither should any agreed property nor the suitability of the product for any specific purpose be deduced from the data contained in the safety data sheet. It is the responsibility of the recipient of the product to ensure any proprietary rights and existing laws and legislation are observed.

SAFETY DATA SHEET

according to Regulation (EC) No. 1907/2006

ARQUAD 12-30

Version 2 Revision Date 23.09.2010 Print Date 10.12.2012 GB / EN

1. IDENTIFICATION OF THE SUBSTANCE/MIXTURE AND OF THE COMPANY/UNDERTAKING

Trade name : ARQUAD 12-30

Use of the Substance/Mixture : Specific use(s): De-emulsifier

Company : Akzo Nobel Surface Chemistry AB
Stenunge Allé 3
SE 444 85 Stenungsund
Sweden

Telephone : +4630385000
Telefax : +4630384659
E-mail address : Regulatory.AffairsSE@akzonobel.com
Emergency telephone number : +31 570679211 (Akzo Nobel Chemicals Deventer, NL) / - Nödtelefon Sverige: KEMIAKUTEN 020-996000

2. HAZARDS IDENTIFICATION

GHS Classification (1272/2008/EC)

Acute toxicity, Category 4
Skin irritation, Category 2
Serious eye damage, Category 1
Acute aquatic toxicity, Category 1

GHS-Labelling (1272/2008/EC)

Symbol(s) :

Signal word : Danger

Hazard statements :

H302	Harmful if swallowed.
H315	Causes skin irritation.
H318	Causes serious eye damage.
H400	Very toxic to aquatic life.

Precautionary statements : **Prevention:**

P273	Avoid release to the environment.

P280	Wear protective gloves/ eye protection/ face protection.
Response:	
P302 + P352	IF ON SKIN: Wash with plenty of soap and water.
P305 + P351 + P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
P308	IF exposed or concerned:
P310	Immediately call a POISON CENTER or doctor/ physician.

Classification (67/548/EEC, 1999/45/EC)

Hazard category: Harmful
Irritant
Dangerous for the environment

Risk advice to man and the environment

Harmful if swallowed.
Irritating to skin.
Risk of serious damage to eyes.
Very toxic to aquatic organisms.

Labelling according to EC Directives 1999/45/EC

Symbol(s) :

Xn Harmful

N Dangerous for the environment

R-phrase(s) :	R22	Harmful if swallowed.
	R38	Irritating to skin.
	R41	Risk of serious damage to eyes.
	R50	Very toxic to aquatic organisms.
S-phrase(s) :	S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
	S37/39	Wear suitable gloves and eye/face protection.
	S57	Use appropriate container to avoid environmental contamination.
	S60	This material and its container must be disposed of as hazardous waste.

Hazardous components which must be listed on the label:

- Dodecyltrimethylammonium chloride

3. COMPOSITION/INFORMATION ON INGREDIENTS

Hazardous substance

Chemical Name	PBT vPvB OEL	CAS-No. EC-No. REACH No.	GHS Classification	Classification	Concentration [%]
Dodecyltrimethylammonium chloride		112-00-5 203-927-0	Acute Tox. 4; H302 Skin Irrit. 2; H315 Eye Dam. 1; H318 Aquatic Acute 1; H400	Xn-N; R22-R38-R41-R50	30 - 40

For the full text of the H-Statements mentioned in this Section, see Section 16.

For the full text of the R-phrases mentioned in this Section, see Section 16.

Non-hazardous substance

Chemical Name	CAS-No. EC-No. REACH No.	Concentration [%]
Water	7732-18-5 231-791-2	60 - 100

4. FIRST AID MEASURES

General advice : Immediate medical attention is required.
Move out of dangerous area.
Show this safety data sheet to the doctor in attendance.

Inhalation : If breathed in, move person into fresh air.

Skin contact : Take off contaminated clothing and shoes immediately.
Rinse immediately with plenty of water.
If skin irritation persists, call a physician.

Eye contact : Rinse with plenty of water.
Get medical attention immediately. Continue to rinse during transport.
Remove contact lenses.
Protect unharmed eye.

Ingestion : Clean mouth with water and drink afterwards plenty of water.
Never give anything by mouth to an unconscious person.
Obtain medical attention.

5. FIRE-FIGHTING MEASURES

Suitable extinguishing media	Use extinguishing measures that are appropriate to local circumstances and the surrounding environment.
Specific hazards during fire fighting / Specific hazards arising from the chemical	Do not allow run-off from fire fighting to enter drains or water courses.
Special protective equipment for fire-fighters	In the event of fire, wear self-contained breathing apparatus.
Further information	Collect contaminated fire extinguishing water separately. This must not be discharged into drains. Fire residues and contaminated fire extinguishing water must be disposed of in accordance with local regulations.

6. ACCIDENTAL RELEASE MEASURES

Personal precautions	For personal protection see section 8. Use personal protective equipment. Ensure adequate ventilation.
Environmental precautions	Do not flush into surface water or sanitary sewer system. If the product contaminates rivers and lakes or drains inform respective authorities.
Methods for cleaning up / Methods for containment	Soak up with inert absorbent material (e.g. sand, silica gel, acid binder, universal binder, sawdust). Keep in suitable, closed containers for disposal.

7. HANDLING AND STORAGE

Handling

Advice on safe handling	For personal protection see section 8. Avoid contact with skin and eyes. Smoking, eating and drinking should be prohibited in the application area. Dispose of rinse water in accordance with local and national regulations.
Advice on protection against fire and explosion	Normal measures for preventive fire protection.

Storage

Requirements for storage areas and containers	Keep container tightly closed in a dry and well-ventilated place.
Other data	No decomposition if stored and applied as directed.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Components with workplace control parameters

Contains no substances with occupational exposure limit values.

Engineering Controls

Effective exhaust ventilation system
Ensure that eyewash stations and safety showers are close to the workstation location.

Personal protective equipment

Respiratory protection	:	In the case of vapour formation use a respirator with an approved filter.
Hand protection	:	Neoprene Nitrile rubber
Eye protection	:	Tightly fitting safety goggles
Skin and body protection	:	Protective suit Choose body protection according to the amount and concentration of the dangerous substance at the work place.
Hygiene measures	:	Handle in accordance with good industrial hygiene and safety practice. When using do not eat or drink. When using do not smoke. Wash hands before breaks and at the end of workday.

Environmental exposure controls

General advice	:	Do not flush into surface water or sanitary sewer system. If the product contaminates rivers and lakes or drains inform respective authorities.

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance

Form	:	liquid
Colour	:	light yellow
Odour	:	Negligible.

Safety data

Flash point	:	100 - 199 °C
Ignition temperature	:	> 100 °C

pH : 6 - 9 at 10 % solution

Melting point/range : < 20 °C

Boiling point/boiling range : 100 °C

Density : 980 kg/m3 at 25 °C

Solubility in other solvents : Soluble in 2-propanol.

Water solubility : soluble

This safety datasheet only contains information relating to safety and does not replace any product information or product specification.

10. STABILITY AND REACTIVITY

Hazardous decomposition products : No hazardous decomposition products are known.

Chemical stability and Hazardous reactions : Note: No decomposition if used as directed.

11. TOXICOLOGICAL INFORMATION

PRODUCT INFORMATION:

Hazard Summary

Inhalation : Inhalation of aerosols may cause irritation to mucous membranes.
Thermal decomposition can lead to release of irritating gases and vapours.

Skin : May cause skin irritation and/or dermatitis.

Eyes : May cause irreversible eye damage.

Ingestion : Harmful if swallowed.
May cause irritation of the mucous membranes.

Toxicology Assessment

Further information : no data available

Test result

Acute oral toxicity : Acute toxicity estimate: 1 666,67 mg/kg

Method: Calculation method

TOXICOLOGY DATA FOR THE COMPONENTS:

Test result

Component: Dodecyltrimethylammonium chloride

Acute oral toxicity : LD50: 300,1 - 2 000 mg/kg
Species: rat
The value is estimated from tests on similar products.

Skin irritation : Result: Irritating to skin.

Eye irritation : Result: Risk of serious damage to eyes.

12. ECOLOGICAL INFORMATION

PRODUCT INFORMATION:

Ecotoxicology Assessment

Additional ecological information : An environmental hazard cannot be excluded in the event of unprofessional handling or disposal.
Very toxic to aquatic organisms.

Test result

Elimination information (persistence and degradability)

Biodegradability : Result: The product contains only readily biodegradable substances.

COMPONENTS:

Test result

Component: Dodecyltrimethylammonium chloride

Ecotoxicity effects

Toxicity to fish : LC50: 1,1 - 10 mg/l
Exposure time: 96 h
Species: Fish
The value is estimated from tests on similar products.

Toxicity to daphnia and other aquatic invertebrates. : EC50: 0,11 - 1 mg/l
Exposure time: 48 h
Species: Daphnia magna (Water flea)
The value is estimated from tests on similar products.

Toxicity to algae : IC50: 0,01 - 0,1 mg/l
Exposure time: 72 h
Species: algae

The value is estimated from tests on similar products.

Elimination information (persistence and degradability)

Biodegradability	Result: Readily biodegradable. (The data are estimated from tests on similar products.) Result: >60% BOD, 28 days, Closed Bottle Test (OECD 301D).

13. DISPOSAL CONSIDERATIONS

Product	The product should not be allowed to enter drains, water courses or the soil. Do not contaminate ponds, waterways or ditches with chemical or used container. Hazardous waste
Contaminated packaging	Empty remaining contents. Dispose of as unused product. Do not re-use empty containers.

14. TRANSPORT INFORMATION

ADR

UN-Number	3082
Proper shipping name	ENVIRONMENTALLY HAZARDOUS SUBSTANCE, LIQUID, N.O.S. (Quarternary alkyl ammonium chloride)
Class	9
Packing group	III
Classification Code	M6
Hazard identification No	90
Labels	9
Tunnel restriction code	(E)
Environmentally hazardous	yes

IATA

UN-Number	3082
Proper shipping name	Environmentally hazardous substance, liquid, n.o.s. (Quarternary alkyl ammonium chloride)
Class	9
Packing group	III
Labels	9
Packing instruction (cargo aircraft)	914
Packing instruction	914

(passenger aircraft)
Packing instruction (LQ) : Y914
Environmentally hazardous : yes

IMDG
UN-Number : 3082
Proper shipping name : ENVIRONMENTALLY HAZARDOUS SUBSTANCE, LIQUID, N.O.S.
(Quarternary alkyl ammonium chloride)
Class : 9
Packing group : III
Labels : 9
EmS Number 1 : F-A
EmS Number 2 : S-F
Marine pollutant : yes
(Quarternary alkyl ammonium chloride)

RID
UN-Number : 3082
Proper shipping name : ENVIRONMENTALLY HAZARDOUS SUBSTANCE, LIQUID, N.O.S.
(Quarternary alkyl ammonium chloride)
Class : 9
Packing group : III
Classification Code : M6
Hazard identification No : 90
Labels : 9
Environmentally hazardous : yes

15. REGULATORY INFORMATION

Other regulations

Major Accident Hazard Legislation : 96/82/EC Update: 2003
Dangerous for the environment
9a
Quantity 1: 100 t
Quantity 2: 200 t

Water contaminating class (Germany) : WGK 3 highly water endangering

Notification status

EINECS : y (positive listing)
On the inventory, or in compliance with the inventory

TSCA : y (positive listing)

On TSCA Inventory

AICS	: y (positive listing) On the inventory, or in compliance with the inventory
DSL	: y (positive listing) All components of this product are on the Canadian DSL list.
ENCS	: y (positive listing) On the inventory, or in compliance with the inventory
KECI	: y (positive listing) On the inventory, or in compliance with the inventory
PICCS	: y (positive listing) On the inventory, or in compliance with the inventory
IECSC	: y (positive listing) On the inventory, or in compliance with the inventory
ISHL	: y (positive listing) On the inventory, or in compliance with the inventory

For explanation of abbreviation see section 16.

Further information

This product is to be considered as a preparation according to EU-legislation.

16. OTHER INFORMATION

Full text of H-Statements referred to under sections 2 and 3.

H302	Harmful if swallowed.
H315	Causes skin irritation.
H318	Causes serious eye damage.
H400	Very toxic to aquatic life.

Full text of R-phrases referred to under sections 2 and 3

R22	Harmful if swallowed.
R38	Irritating to skin.
R41	Risk of serious damage to eyes.
R50	Very toxic to aquatic organisms.

Explanations for possible abbreviations mentioned in section 2

PBT : PBT: Persistent, bioaccumulative and toxic.
vPvB : vPvB: Very persistent and very bioaccumulative.
OEL : OEL: Occupational exposure limit.

Notification status explanation

EINECS	European Inventory of Existing Commercial Chemical Substances (EINECS)

TSCA	TSCA Inventory
AICS	Australia Inventory of Chemical Substances (AICS)
DSL	Domestic Substances List (DSL)
ENCS	Japan. ENCS - Existing and New Chemical Substances Inventory
KECI	Korea. Korean Exisiting Chemicals Inventory (KECI)
PICCS	Inventory of Chemicals and Chemical Substances (PICCS)
IECSC	China. Inventory of Existing Chemical Substances in China (IECSC)
ISHL	Industrial Safety and Health Law OEL

The information provided in this Safety Data Sheet is correct to the best of our knowledge, information and belief at the date of its publication. The information given is designed only as a guidance for safe handling, use, processing, storage, transportation, disposal and release and is not to be considered a warranty or quality specification. The information relates only to the specific material designated and may not be valid for such material used in combination with any other materials or in any process, unless specified in the text.

Material Safety Data Sheet

MSDS# 15-03922

Section 1. Chemical Product and Company Identification

Product name **AROMOX® C/12W**

Material Uses : Surfactant.

Supplier/ Manufacturer

AKZO NOBEL SURFACE CHEMISTRY LLC
525 West Van Buren
Chicago, IL 60607-3823
www.surfactants.akzonobel.com

AKZO NOBEL CHEMICALS LTD.
1 City Centre Drive, Suite 318
Mississauga, Ontario L5B 1M2
Canada

In Case of Emergency

CHEMTREC:	800-424-9300
CANUTEC:	613-996-6666
Medical/Handling:	914-693-6946
Product/Technical:	800-906-9977

Section 2. Hazards Identification

Physical State	Liquid.
Color	Clear.
Odor	Bland.

Emergency Overview

WARNING!
CAUSES SEVERE EYE IRRITATION.
TOXIC TO AQUATIC ORGANISMS.
MAY BE HARMFUL IF SWALLOWED.
POSSIBLE CANCER HAZARD
CONTAINS MATERIAL WHICH MAY CAUSE CANCER BASED ON ANIMAL DATA.
MAY BE HARMFUL TO ENVIRONMENT IF RELEASED IN LARGE AMOUNTS.

Risk of cancer depends on duration and level of exposure. Avoid contact with eyes. Do not ingest. Wash thoroughly after handling. Avoid contact of spilled material and runoff with soil and surface waterways.

Routes of Entry Absorbed through skin. Eye contact.

See Toxicological Information (section 11)

Section 3. Composition/ Information on Ingredients

Name	CAS #	% by Weight
Ethanol,2,2'-iminobis-,N-coco alkyl derivs., N-oxides	61791-47-7	28-34
water	7732-18-5	66-72
Ethanol, 2,2'-iminobis-, n-coco alkyl derivs.	61791-31-9	1
hydrogen peroxide solution	7722-84-1	<0.34

Section 4. First Aid Measures

Eye Contact	Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 30 minutes. Cold water may be used. Get medical attention immediately.
Skin Contact	Wash with soap and water. Get medical attention if irritation develops. Cold water may be used.
Inhalation	If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.

Continued on Next Page

Ingestion	Do NOT induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. If large quantities of this material are swallowed, call a physician immediately. Loosen tight clothing such as a collar, tie, belt or waistband.
Medical Conditions Aggravated by Overexposure:	Repeated exposure to a highly toxic material may produce general deterioration of health by an accumulation in one or many human organs.

Section 5. Fire Fighting Measures

Flammability of the Product	May be combustible at high temperature.
Flash Points	Closed cup: >100°C (212°F).
Products of Combustion	These products are carbon oxides (CO, CO$_2$), nitrogen oxides (NO, NO$_2$...).
Fire Fighting Media and Instructions	SMALL FIRE: Use DRY chemical powder. LARGE FIRE: Use water spray, fog or foam. Do not use water jet.
Protective Clothing (Fire)	Be sure to use an approved/certified respirator or equivalent.

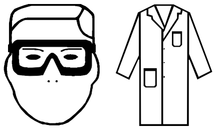
Section 6. Accidental Release Measures

Small Spill and Leak	Dilute with water and mop up, or absorb with an inert dry material and place in an appropriate waste disposal container. Finish cleaning by spreading water on the contaminated surface and dispose of according to local and regional authority requirements.
Large Spill and Leak	Absorb with an inert material and put the spilled material in an appropriate waste disposal. Finish cleaning by spreading water on the contaminated surface and allow to evacuate through the sanitary system.

Section 7. Handling and Storage

Handling	Avoid contact with eyes. Do not ingest. Wash thoroughly after handling. Avoid contact of spilled material and runoff with soil and surface waterways.
Storage	Keep container tightly closed. Keep container in a cool, well-ventilated area.

Section 8. Exposure Controls/ Personal Protection

Engineering Controls	Provide exhaust ventilation or other engineering controls to keep the airborne concentrations of vapors below their respective occupational exposure limits. Ensure that eyewash stations and safety showers are proximal to the work-station location.
Personal Protection	
Eyes	Splash goggles.
Body	Lab coat.
Respiratory	Wear appropriate respirator when ventilation is inadequate.
Hands	Not applicable.
Feet	Suitable protective footwear.
Protective Clothing (Pictograms)	
Personal Protection in Case of a Large Spill	Splash goggles. Full suit. Boots. Gloves. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.

Ingredient Name	**Exposure Limits United States**

Continued on Next Page

Ethanol,2,2'-iminobis-,N-coco alkyl derivs., N-oxides	Not available.
water	Not available.
Ethanol, 2,2'-iminobis-, n-coco alkyl derivs.	Not available.
hydrogen peroxide solution	**ACGIH TLV (United States, 2005). Notes: 1996 Adoption Refers to Appendix A -- Carcinogens.** TWA: 1.4 mg/m^3 8 hour(s). Form: All forms TWA: 1 ppm 8 hour(s). Form: All forms **NIOSH REL (United States, 2001).** TWA: 1.4 mg/m^3 10 hour(s). Form: All forms TWA: 1 ppm 10 hour(s). Form: All forms **OSHA PEL (United States, 1997).** TWA: 1.4 mg/m^3 8 hour(s). Form: All forms TWA: 1 ppm 8 hour(s). Form: All forms **OSHA PEL 1989 (United States, 1989).** TWA: 1.4 mg/m^3 8 hour(s). Form: All forms TWA: 1 ppm 8 hour(s). Form: All forms

Section 9. Physical and Chemical Properties

Physical State	Liquid.
Color	Clear.
Odor	Bland.
pH	6.5 to 8 [Neutral.]
Boiling/Condensation Point	The lowest known value is 80°C (176°F) (Ethanol,2,2'=iminobis-,n-coco alkyl derivs., n-oxides). Weighted average: 95.52°C (203.9°F)
Melting/Freezing Point	May start to solidify at 6°C (42.8°F) based on data for: Ethanol, 2,2'-iminobis-, n-coco alkyl derivs.. Weighted average: -5.77°C (21.6°F)
Pour Point	0ºC
Density	The only known value is 1 g/cm^3 (water).
Vapor Pressure	The highest known value is <2.7 kPa (<20 mmHg) (at 20°C) (Ethanol,2,2'=iminobis-,n-coco alkyl derivs., n-oxides). Weighted average: 2.4 kPa (18 mmHg) (at 20°C)
Evaporation Rate	The highest known value is <1 (Ethanol,2,2'=iminobis-,n-coco alkyl derivs., n-oxides) Weighted average: 0.53compared to Butyl acetate.
Solubility	Easily soluble in cold water, hot water, methanol, acetone.
Dispersion Properties	See solubility in water, methanol, acetone.
Physical Chemical Comments	Viscosity=345cP@25ºC

Section 10. Stability and Reactivity

Stability and Reactivity	The product is stable.
Conditions of Instability	**Ethanol,2,2'=iminobis-,n-coco alkyl derivs., n-oxides**: S33- Take precautionary measures against static discharges.
Incompatibility with Various Substances	Reactive with OXIDIZING AGENTS.
Hazardous Polymerization	Will not occur.

Section 11. Toxicological Information

Toxicity to Animals

Ingredient Name or Product name	Test	Result	Route	Species

Ethanol,2,2'-iminobis-,N-coco alkyl derivs., N-oxides	LD50	1080 mg/kg	Oral	Rat based on data for: (similar material)
Ethanol, 2,2'-iminobis-, n-coco alkyl derivs.	LD50	6600 mg/kg	Oral	Rat based on data for: (similar material)
hydrogen peroxide solution	LD50	376 mg/kg	Oral	Rat
	LD50	910 mg/kg	Oral	Rat
	LD50	1518 mg/kg	Oral	Rat
	LD50	4060 mg/kg	Dermal	Rat
	LD50	1072 mg/kg	Dermal	Mouse
	LDLo	1429 mg/kg	Oral	man
	LDLo	8500 mg/kg	Oral	child
	LDLo	500 mg/kg	Dermal	Rabbit

Special Remarks on Toxicity to Animals **Ethanol, 2,2'-iminobis-, n-coco alkyl derivs.**: INHALATION LC50 = 88 ppm @ 1 hour(s) Rat

Chronic Effects on Humans **CARCINOGENIC EFFECTS**: Classified A3 (Proven for animal.) by ACGIH [hydrogen peroxide solution]. Classified 3 (Not classifiable for human.) by IARC [hydrogen peroxide solution].

Acute Effects Skin Slightly irritating to the skin.

Acute Effects Eyes Severely irritating to the eyes.

Section 12. Ecological Information

Ecotoxicity

Ingredient Name or Product name	Species	Period	Result
Ethanol,2,2'-iminobis-,N-coco alkyl derivs., N-oxides	Zebrafish based on data for: (similar material) (LC50)	96 hour(s)	3.4 mg/l
	daphnia based on data for: (similar material) (EC50)	48 hour(s)	1.1 mg/l
Ethanol, 2,2'-iminobis-, n-coco alkyl derivs.	Fish (LC50)	96 hour(s)	0.28 mg/l
	Daphnia (EC50)	48 hour(s)	0.84 mg/l
hydrogen peroxide solution	Daphnia magna (EC50)	48 hour(s)	24 mg/l
	Oncorhynchus mykiss (LC50)	96 hour(s)	22 mg/l
	Lepomis macrochirus (LC50)	96 hour(s)	26.7 mg/l

Biodegradability and Ecotoxicity Remarks **Ethanol,2,2'=iminobis-,n-coco alkyl derivs., n-oxides**: 57% @ 28 day(s) CBT based on data for: (similar material)
Ethanol, 2,2'-iminobis-, n-coco alkyl derivs.: 60% @ 28 day(s) CBT based on data for: (similar material)

Products of Degradation These products are carbon oxides (CO, CO_2) and water, nitrogen oxides (NO, NO_2...).

Section 13. Disposal Considerations

Waste Information Waste must be disposed of in accordance with federal, state and local environmental control regulations.

RCRA Classification Not a RCRA hazardous waste.

Consult your local or regional authorities.

Section 14. Transport Information

Regulatory Information	UN number	Proper shipping name	Class	Packing Group	Label	Additional information
DOT Classification	Not regulated.	-	- -	-		-
TDG Classification	Not regulated.	-	- -	-		-

Continued on Next Page

IMDG Class	Not regulated.	-	- -	-		-
IATA-DGR Class	Not regulated.	-	- -	-		-

Section 15. Regulatory Information

HCS Classification

Irritating material

U.S. Federal Regulations

TSCA: All intentionally present components are listed on the TSCA inventory.

DSL: All intentionally present components are listed on the DSL.

TSCA 5(a)2 final significant rules: No products were found.

CERCLA: Hazardous substances.: No products were found.

SARA 302/304/311/312 extremely hazardous substances: No products were found.
SARA 302/304 emergency planning and notification: No products were found.
SARA 302/304/311/312 hazardous chemicals: AROMOX® C/12W
SARA 311/312 MSDS distribution - chemical inventory - hazard identification: AROMOX® C/12W: Immediate (Acute) Health Hazard

SARA 313 Form R Reporting Requirements
No products were found.

SARA 313 Supplier Notification
No products were found.

State Regulations

Pennsylvania RTK: hydrogen peroxide solution: (environmental hazard, generic environmental hazard)
Massachusetts RTK: hydrogen peroxide solution
New Jersey: hydrogen peroxide solution

California prop. 65: No products were found.

WHMIS (Canada)

Class D-2B: Material causing other toxic effects (TOXIC).

CEPA DSL: Ethanol,2,2'=iminobis-,n-coco alkyl derivs., n-oxides; water; Ethanol, 2,2'-iminobis-, n-coco alkyl derivs.; hydrogen peroxide solution

	Component	**EC Number**	**EC Status**	**EC Annex**
European Union	Ethanol,2,2'-iminobis-,N-coco alkyl derivs., N-oxides	263-180-1	Not available.	Not available.
	water	231-791-2	Not available.	Not available.
	Ethanol, 2,2'-iminobis-, n-coco alkyl derivs.	263-163-9	Not available.	Not available.
	hydrogen peroxide solution	231-765-0	Not available.	008-003-00-9

Other International Lists

Australia (NICNAS): Ethanol,2,2'=iminobis-,n-coco alkyl derivs., n-oxides; water; Ethanol, 2,2'-iminobis-, n-coco alkyl derivs.; hydrogen peroxide solution

China: water; Ethanol, 2,2'-iminobis-, n-coco alkyl derivs.; hydrogen peroxide solution

Germany water class: Ethanol, 2,2'-iminobis-, n-coco alkyl derivs.; hydrogen peroxide solution

Japan (MITI): water; hydrogen peroxide solution

Korea (TCCL): Ethanol,2,2'=iminobis-,n-coco alkyl derivs., n-oxides; water; Ethanol, 2,2'-iminobis-, n-coco alkyl derivs.; hydrogen peroxide solution

Continued on Next Page

Philippines (RA6969): water; Ethanol, 2,2'-iminobis-, n-coco alkyl derivs.; hydrogen peroxide solution

Section 16. Other Information

Hazardous Material Information System (U.S.A.)

Health	2
Fire Hazard	1
Physical Hazards	0
Personal Protection	

National Fire Protection Association (U.S.A.)

Other Information Aromox® is a registered trademark of Akzo Nobel or affiliated companies and is registered in one or more countries including the United States.

Validation Date	**5/25/2010.**	**Validated by**	**Product Safety Specialist**
Previous Validation Date	5/14/2007.	**Print Date**	5/25/2010.
		Phone Number	**312-544-7038**

Notice to Reader

The information in the material safety data sheet should be provided to all who will use, handle, store, transport or otherwise be exposed to this product. All information concerning this product and/or suggestions for handling and use contained herein are offered in good faith and are believed to be reliable as of the date of publication. However, no warranty is made as to the accuracy of and/or sufficiency of such information and/or suggestions or as to the product's merchantability or fitness for any particular purpose, or that any suggested use will not infringe any patent. Nothing contained herein shall be construed as granting or extending any license under any patent. Buyer must determine for himself, by preliminary tests or otherwise, the suitability of this product for his purposes, including mixing with other products. The information contained herein supersedes all previously issued bulletins on the subject matter covered. If the date on this document is more than three years old, call to make certain that this sheet is current.

SIGMA-ALDRICH

sigma-aldrich.com

SAFETY DATA SHEET

according to Regulation (EC) No. 1907/2006
Version 4.4 Revision Date 14.06.2010
Print Date 16.07.2010

1. IDENTIFICATION OF THE SUBSTANCE/MIXTURE AND OF THE COMPANY/UNDERTAKING

Product name : Sodium dodecyl sulfate

Product Number : 436143
Brand : Sigma-Aldrich

Company : Sigma-Aldrich Company Ltd.
The Old Brickyard
NEW ROAD, GILLINGHAM
Dorset
SP8 4XT
UNITED KINGDOM
Telephone : +441747833000
Fax : +441747833313
Emergency Phone # : +44 (0)1747 833100
E-mail address : eurtechserv@sial.com

2. HAZARDS IDENTIFICATION

Classification of the substance or mixture

According to Regulation (EC) No1272/2008
Flammable solids (Category 1)
Acute toxicity, Dermal (Category 3)
Acute toxicity, Oral (Category 4)
Skin irritation (Category 2)
Eye irritation (Category 2)
Specific target organ toxicity - single exposure (Category 3)

According to European Directive 67/548/EEC as amended.
Highly flammable. Harmful in contact with skin and if swallowed. Irritating to eyes, respiratory system and skin.

Label elements

Pictogram

Signal word Danger

Hazard statement(s)

H228	Flammable solid.
H302	Harmful if swallowed.
H311	Toxic in contact with skin.
H315	Causes skin irritation.
H319	Causes serious eye irritation.
H335	May cause respiratory irritation.

Precautionary statement(s)

P210	Keep away from heat/sparks/open flames/hot surfaces. - No smoking.
P261	Avoid breathing dust/fume/gas/mist/vapours/spray.
P280	Wear protective gloves/protective clothing.
P305 + P351 + P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
P312	Call a POISON CENTER or doctor/physician if you feel unwell.

Hazard symbol(s)	
F	Highly flammable
Xn	Harmful

R-phrase(s)	
R11	Highly flammable.
R21/22	Harmful in contact with skin and if swallowed.
R36/37/38	Irritating to eyes, respiratory system and skin.

S-phrase(s)	
S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S36/37	Wear suitable protective clothing and gloves.

Other hazards - none

3. COMPOSITION/INFORMATION ON INGREDIENTS

Synonyms : Lauryl sulfatesodium salt
Sodium lauryl sulfate
Dodecyl sodium sulfate
Dodecyl sulfatesodium salt
SDS

Formula : $C_{12}H_{25}NaO_4S$
Molecular Weight : 288.38 g/mol

CAS-No.	EC-No.	Index-No.	Classification	Concentration
Sodium dodecyl sulphate				
151-21-3	205-788-1	-	Flam. Sol. 1; Acute Tox. 3; Acute Tox. 4; Skin Irrit. 2; Eye Irrit. 2; STOT SE 3; H228, H302, H311, H315, H319, H335 F, Xn, R11 - R21/22 - R36/37/38	-

For the full text of the H-Statements mentioned in this Section, see Section 16.

4. FIRST AID MEASURES

General advice
Consult a physician. Show this safety data sheet to the doctor in attendance.

If inhaled
If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.

In case of skin contact
Wash off with soap and plenty of water. Take victim immediately to hospital. Consult a physician.

In case of eye contact
Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician.

If swallowed
Do NOT induce vomiting. Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.

5. FIRE-FIGHTING MEASURES

Suitable extinguishing media
Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

Special protective equipment for fire-fighters
Wear self contained breathing apparatus for fire fighting if necessary.

Further information
Use water spray to cool unopened containers.

6. ACCIDENTAL RELEASE MEASURES

Personal precautions
Wear respiratory protection. Avoid dust formation. Avoid breathing vapors, mist or gas. Ensure adequate ventilation. Remove all sources of ignition. Evacuate personnel to safe areas. Avoid breathing dust.

Environmental precautions
Prevent further leakage or spillage if safe to do so. Do not let product enter drains. Discharge into the environment must be avoided.

Methods and materials for containment and cleaning up
Sweep up and shovel. Contain spillage, and then collect with an electrically protected vacuum cleaner or by wet-brushing and place in container for disposal according to local regulations (see section 13). Keep in suitable, closed containers for disposal. Contain spillage, pick up with an electrically protected vacuum cleaner or by wet-brushing and transfer to a container for disposal according to local regulations (see section 13).

7. HANDLING AND STORAGE

Precautions for safe handling
Avoid contact with skin and eyes. Avoid formation of dust and aerosols.
Provide appropriate exhaust ventilation at places where dust is formed. Keep away from sources of ignition - No smoking. Take measures to prevent the build up of electrostatic charge.

Conditions for safe storage
Keep container tightly closed in a dry and well-ventilated place. Store in cool place.

hygroscopic

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Contains no substances with occupational exposure limit values.

Personal protective equipment

Respiratory protection
Where risk assessment shows air-purifying respirators are appropriate use a full-face particle respirator type N100 (US) or type P3 (EN 143) respirator cartridges as a backup to engineering controls. If the respirator is the sole means of protection, use a full-face supplied air respirator. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

Hand protection
Handle with gloves. Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.

The selected protective gloves have to satisfy the specifications of EU Directive 89/686/EEC and the standard EN 374 derived from it.

Eye protection
Face shield and safety glasses Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU).

Skin and body protection
Complete suit protecting against chemicals, Flame retardant antistatic protective clothing, The type of protective equipment must be selected according to the concentration and amount of the dangerous substance at the specific workplace.

Hygiene measures
Avoid contact with skin, eyes and clothing. Wash hands before breaks and immediately after handling the product.

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance

Form	solid
Colour	white

Safety data

pH	7.2
Melting point	204 - 207 °C - lit.
Boiling point	no data available
Flash point	no data available
Flammability (solid, gas)	The substance or mixture is a flammable solid with the subcategory 1.
Ignition temperature	no data available
Lower explosion limit	no data available
Upper explosion limit	no data available
Density	0.370 g/cm3
Water solubility	soluble
Partition coefficient: n-octanol/water	log Pow: 1.6

10. STABILITY AND REACTIVITY

Chemical stability
Stable under recommended storage conditions.

Conditions to avoid
Heat, flames and sparks. Extremes of temperature and direct sunlight.

Materials to avoid
Oxidizing agents

Hazardous decomposition products
Hazardous decomposition products formed under fire conditions. - Carbon oxides, Sulphur oxides, Sodium oxides

11. TOXICOLOGICAL INFORMATION

Acute toxicity
LD50 Oral - rat - 1,288 mg/kg

LC50 Inhalation - rat - 1 h - > 3,900 mg/m3

LD50 Dermal - rabbit - 580 mg/kg

Skin corrosion/irritation
Skin - rabbit - Skin irritation - 24 h

Serious eye damage/eye irritation
Eyes - rabbit - Eye irritation

Respiratory or skin sensitization
Prolonged or repeated exposure may cause allergic reactions in certain sensitive individuals.

Germ cell mutagenicity
no data available

Carcinogenicity

IARC: No component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.

Reproductive toxicity
no data available

Specific target organ toxicity - single exposure
Inhalation - May cause respiratory irritation.

Specific target organ toxicity - repeated exposure
no data available

Aspiration hazard
no data available

Potential health effects

Inhalation	May be harmful if inhaled. Causes respiratory tract irritation.
Ingestion	Harmful if swallowed.
Skin	Toxic if absorbed through skin. Causes skin irritation.
Eyes	Causes serious eye irritation.

Signs and Symptoms of Exposure
sneezing, The sodium salt of dodecyl sulfate has been reported to cause pulmonary sensitization resulting in hyperactive airway dysfunction and pulmonary allergy accompanied by fatigue, malaise, and aching. Significant symptoms of exposure can persist for more than two years and can be activated by a variety of nonspecific environmental stimuli such as automobile exhaust, perfumes, and passive smoking.

Additional Information
RTECS: WT1050000

12. ECOLOGICAL INFORMATION

Toxicity

Toxicity to fish	mortality NOEC - Oncorhynchus mykiss (rainbow trout) - 19.5 mg/l - 96 h
	mortality LOEC - Pimephales promelas (fathead minnow) - 4.6 mg/l - 8 d
	LC50 - Oncorhynchus mykiss (rainbow trout) - 3.6 mg/l - 96 h
Toxicity to algae	Growth inhibition LOEC - Pseudokirchneriella subcapitata - 2.68 mg/l - 6 d

Persistence and degradability
no data available

Bioaccumulative potential

Bioaccumulation	Cyprinus carpio (Carp) - 72 h Bioconcentration factor (BCF): 3.9 - 5.3

Mobility in soil
no data available

PBT and vPvB assessment
no data available

Other adverse effects
Toxic to aquatic life.
no data available

13. DISPOSAL CONSIDERATIONS

Product
Contact a licensed professional waste disposal service to dispose of this material. Burn in a chemical incinerator equipped with an afterburner and scrubber but exert extra care in igniting as this material is highly flammable. Offer surplus and non-recyclable solutions to a licensed disposal company.

Contaminated packaging
Dispose of as unused product.

14. TRANSPORT INFORMATION

ADR/RID
UN-Number: 2926 Class: 4.1 (6.1) Packing group: II
Proper shipping name: FLAMMABLE SOLID, TOXIC, ORGANIC, N.O.S. (Sodium dodecyl sulphate)

IMDG
UN-Number: 2926 Class: 4.1 (6.1) Packing group: II EMS-No: F-A, S-G
Proper shipping name: FLAMMABLE SOLID, TOXIC, ORGANIC, N.O.S. (Sodium dodecyl sulphate)
Marine pollutant: No

IATA
UN-Number: 2926 Class: 4.1 (6.1) Packing group: II
Proper shipping name: Flammable solid, toxic, organic, n.o.s. (Sodium dodecyl sulphate)

15. REGULATORY INFORMATION

This safety datasheet complies with the requirements of Regulation (EC) No. 1907/2006.

16. OTHER INFORMATION

Text of H-code(s) and R-phrase(s) mentioned in Section 3

Acute Tox.	Acute toxicity
Eye Irrit.	Eye irritation
Flam. Sol.	Flammable solids
H228	Flammable solid.
H302	Harmful if swallowed.
H311	Toxic in contact with skin.
H315	Causes skin irritation.
H319	Causes serious eye irritation.
H335	May cause respiratory irritation.
Skin Irrit.	Skin irritation
F	Highly flammable
Xn	Harmful
R11	Highly flammable.
R21/22	Harmful in contact with skin and if swallowed.
R36/37/38	Irritating to eyes, respiratory system and skin.

Further information

The above information is believed to be correct but does not purport to be all inclusive and shall be used only as a guide. The information in this document is based on the present state of our knowledge and is applicable to the product with regard to appropriate safety precautions. It does not represent any guarantee of the properties of the product. Sigma-Aldrich Co., shall not be held liable for any damage resulting from handling or from contact with the above product. See reverse side of invoice or packing slip for additional terms and conditions of sale.

Safety Data Sheet

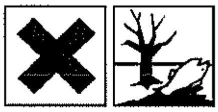
according to 1907/2006/EC, Article 31

1 Identification of the substance/preparation and of the company/undertaking

- **Product details**
- **Trade name:** **Imbentin-AG/124S/040**
- **Application of the substance / the preparation** Non-ionic surfactant
- **Manufacturer/Supplier:**
  Dr. W. Kolb AG
  Maienbrunnenstrasse 1
  P.O. Box 64
  CH-8908 Hedingen
  Switzerland
  Phone +4144 762 4646
  Fax +4144 762 4600
- **Further information obtainable from:**
  Regulatory Affairs
  +4144 762 4733
  E-mail: product.safety@kolb.ch
- **Only representative (according to Art. 8 of Regulation (EC) 1907/2006)**
  Dr. W. Kolb Nederland B.V.
  Postbus 123
  NL-4790 AC Klundert
  E-Mail: reach@kolb.ch
- **Information in case of emergency:**
  Phone (24 h): +4144 466 6448
  Fax (24 h): +4144 466 6660

2 Hazards identification

- **Hazard description:**



Xi Irritant
N Dangerous for the environment

- **Information concerning particular hazards for human and environment:**
  R 41 Risk of serious damage to eyes.
  R 50 Very toxic to aquatic organisms.

3 Composition/information on ingredients

- **Chemical characterization:** Alcohol C12-14 + 4 EO
- **CAS No.:**
  68439-50-9 Alcohols C12-14, ethoxylated
- **INCI:** C12-14 pareth-4
- **EINECS:** Polymer

4 First aid measures

- **After inhalation:** Supply fresh air; consult doctor in case of complaints.
- **After skin contact:**
  Rinse with warm water.
  If skin irritation continues, consult a doctor.
- **After eye contact:** Rinse opened eye for several minutes under running water. Then consult a doctor.

(Contd. on page 2)

(Contd. of page 1)

- **After swallowing:** Seek medical treatment.

5 Fire-fighting measures

- **Suitable extinguishing agents:**
  CO2, powder or water spray. Fight larger fires with water spray or alcohol resistant foam.
- **Protective equipment:** No special measures required.

6 Accidental release measures

- **Person-related safety precautions:** Not required.
- **Measures for environmental protection:**
  Inform respective authorities in case of seepage into water course or sewage system.
  Do not allow to enter sewers/ surface or ground water.
- **Measures for cleaning/collecting:**
  Absorb with liquid-binding material (sand, diatomite, acid binders, universal binders, sawdust).
  Dispose contaminated material as waste according to item 13.

7 Handling and storage

- **Handling:**
- **Information for safe handling:** No special precautions are necessary if used correctly.
- **Information about fire - and explosion protection:** No special measures required.

- **Storage:**
- **Requirements to be met by storerooms and receptacles:** No special requirements.
- **Information about storage in one common storage facility:** Not required.
- **Further information about storage conditions:** Keep container tightly sealed.

8 Exposure controls/personal protection

- **Additional information about design of technical facilities:** No further data; see item 7.

- **Ingredients with limit values that require monitoring at the workplace:** Not required.
- **Additional information:** The lists valid during the making were used as basis.

- **Personal protective equipment:**
- **General protective and hygienic measures:**
  Keep away from foodstuffs, beverages and feed.
  Immediately remove all soiled and contaminated clothing
  Wash hands before breaks and at the end of work.
  Avoid contact with the eyes.
- **Respiratory protection:** Not required.
- **Protection of hands:**

Protective gloves

The glove material has to be impermeable and resistant to the product/ the substance/ the preparation.
Due to missing tests no recommendation to the glove material can be given for the product/ the preparation/ the chemical mixture.
Selection of the glove material on consideration of the penetration times, rates of diffusion and the degradation

- **Material of gloves**
  The selection of the suitable gloves does not only depend on the material, but also on further marks of quality and varies from manufacturer to manufacturer.
- **Penetration time of glove material**
  The exact break through time has to be found out by the manufacturer of the protective gloves and has to be observed.

(Contd. on page 3)

(Contd. of page 2)

· **Eye protection:**

Tightly sealed goggles

*

9 Physical and chemical properties

· **General Information**	
Form:	Fluid
Colour:	Colourless
Odour:	Nearly odourless
· **Change in condition**	
Setting temperature / range:	~ 5°C
· **Flash point:**	> 100°C
· **Density:**	(25°C) ~ 0.95 g/cm^3
· **pH-value:**	~ 6 (10% H2O)
· **Viscosity:**	
Dynamic:	(25°C) ~ 30 mPa.s

10 Stability and reactivity

· **Thermal decomposition / conditions to be avoided:** No decomposition if used according to specifications.
· **Dangerous reactions** No dangerous reactions known.
· **Dangerous decomposition products:** No dangerous decomposition products known.

11 Toxicological information

· **Acute toxicity:**

· **LD/LC50 values relevant for classification:**		
Oral	LD50	> 2000 mg/kg (rat)

· **Primary irritant effect:**
· **on the skin:** No irritating effect.
· **on the eye:** Strong irritant with the danger of severe eye injury.
· **Sensitization:** No sensitizing effects known.

*

12 Ecological information

· **Ecotoxical effects:**

· **Acquatic toxicity:**	
EC50	< 1 mg/l (literature data)

· **General notes:**
Very toxic for aquatic organisms
Do not allow product to reach ground water, water course or sewage system.
Danger to drinking water if even small quantities leak into the ground.
This surfactant complies with the biodegradability criteria as laid down in Regulation (EC) No.648/2004 on detergents. Data to support this assertion are held at the disposal of the competent authorities of the Member States and will be made available to them, at their direct request or at the request of a detergent manufacturer.
Water hazard class 2 (German Regulation) (Assessment by list): hazardous for water

(Contd. on page 4)

(Contd. of page 3)

13 Disposal considerations

- **Product:**
- **Recommendation**
  Must not be disposed together with household garbage. Do not allow product to reach sewage system.

· **European waste catalogue**	
16 03 05	organic wastes containing dangerous substances

- **Uncleaned packaging:**
- **Recommendation:** Disposal must be made according to official regulations.

14 Transport information

- **Land transport ADR/RID (cross-border)**

- **ADR/RID class:** 9 Miscellaneous dangerous substances and articles.
- **Danger code (Kemler):** 90
- **UN-Number:** 3082
- **Packaging group:** III
- **Hazard label:** 9
- **Description of goods:** 3082 ENVIRONMENTALLY HAZARDOUS SUBSTANCE, LIQUID, N.O.S. (Surfactant)

- **Maritime transport IMDG:**

- **IMDG Class:** 9
- **UN Number:** 3082
- **Label** 9
- **Packaging group:** III
- **EMS Number:** F-A,S-F
- **Marine pollutant:** Yes
- **Proper shipping name:** ENVIRONMENTALLY HAZARDOUS SUBSTANCE, LIQUID, N.O.S. (Surfactant)

- **Air transport ICAO-TI and IATA-DGR:**

- **ICAO/IATA Class:** 9
- **UN/ID Number:** 3082
- **Label** 9
- **Packaging group:** III
- **Proper shipping name:** ENVIRONMENTALLY HAZARDOUS SUBSTANCE, LIQUID, N.O.S. (Surfactant)

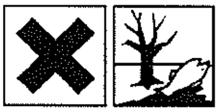
15 Regulatory information

- **Labelling according to EU guidelines:** Classification and labelling according to CESIO recommendations

(Contd. on page 5)

(Contd. of page 4)

- **Code letter and hazard designation of product:**



Xi Irritant
N Dangerous for the environment

- **Risk phrases:**
  41 Risk of serious damage to eyes.
  50 Very toxic to aquatic organisms.
- **Safety phrases:**
  26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
  39 Wear eye/face protection.
  61 Avoid release to the environment. Refer to special instructions/safety data sheets.
- **Pre-registration according to Regulation (EC) 1907/2006 (Reach)**
  This product is a polymer as defined in Art. 3 (5) of the Reach regulation and is exempt from pre-registration and registration. We confirm that all monomers and other reactants have been pre-registered by Kolb and/or our suppliers. Substances imported from Switzerland have been pre-registered by our only representative (see section 1 of this SDS).

16 Other information

This information is based on our present knowledge. However, this shall not constitute a guarantee for any specific product features and shall not establish a legally valid contractual relationship.

- **Department issuing MSDS:** Regulatory Affairs
- **Contact:** E-mail: product.safety@kolb.ch
- *** Data compared to the previous version altered.**

APPENDIX I: WBM test results for compatibility evaluation.

DRILLING FLUID FORMULATIONS AND TEST RESULTS

SAMPLE INFO		
REQUEST NO	**Master project Carina Robberstad**	Confidential
FLUID SYSTEM	**Glydril 1,1 SG**	
DESCRIPTION	**WBM**	
TEST DATE	**13.09.12-18.09.12**	
TESTED BY	**Carina Robberstad**	

SAMPLE COMPOSITION												
Sample												
Mixing / Testing date												
Mixing volume			**1000mL**									
Freshwater		g/l	921,5									
KCl	MIN 11-087	g/l	50									
Soda Ash	MIN 08-270	g/l	1									
Polypac ELV	MIN 08-442	g/l	15									
Duotec NS	MIN 11-090	g/l	3									
Glydril MC	MIN 11-099	g/l	20									
Barite (reg)	MIN 12-055	g/l	89,5									
		g/l										
		g/l										
		g/l										
		g/l										
		g/l										

AGING CONDITIONS											
Period aged	HOURS		**16**	**16**	**16**						
Temperature	ºC		**100**	**100**	**100**						
Dynamic / Static	D/S		**D**	**D**	**D**						

RHEOLOGY		**BHR**	**AHR**	**AHR**	**AHR**						
Temperature	ºC	**50**	**2**	**20**	**50**	**50**	**50**	**50**	**50**	**50**	**50**
600 rpm	lbs/100ft²	34	83	52	31						
300 rpm	lbs/100ft²	23	52	34	21						
200 rpm	lbs/100ft²	18	40	26	17						
100 rpm	lbs/100ft²	12	26	18	12						
6 rpm	lbs/100ft²	4	7	5	4						
3 rpm	lbs/100ft²	3	6	4	3						
10 second gel	lbs/100ft²		7	5	4						
10 minute gel	lbs/100ft²		10	8	6						
Plastic Viscosity	cP	11	31	18	10	0	0	0	0	0	0
Yield Point	lbs/100ft²	12	21	16	11	0	0	0	0	0	0

FILTRATION - API											
API	ml			5,9							

pH		9,7		8,6							
Specific gravity	sg			1,10							

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DRILLING FLUID FORMULATIONS AND TEST RESULTS

SAMPLE INFO		
REQUEST NO	**Master project Carina Robberstad**	Confidential
FLUID SYSTEM	**Glydril 1,1 SG with 12000ppm Luvicap 55w**	
DESCRIPTION	**WBM**	
TEST DATE	**13.09.12-18.09.12**	
TESTED BY	**Carina Robberstad**	

SAMPLE COMPOSITION												
Sample												
Mixing / Testing date												
Mixing volume			**1000mL**									
Freshwater		g/l	921,5									
KCl	MIN 11-087	g/l	50									
Soda Ash	MIN 08-270	g/l	1									
Polypac ELV	MIN 08-442	g/l	15									
Duotec NS	MIN 11-090	g/l	3									
Glydril MC	MIN 11-099	g/l	20									
Barite (reg)	MIN 12-055	g/l	89,5									
		g/l										
Luvicap 55w		g/l	12									
		g/l										
		g/l										
		g/l										

AGING CONDITIONS											
Period aged	HOURS		**16**	**16**	**16**						
Temperature	ºC		**100**	**100**	**100**						
Dynamic / Static	D/S		**D**	**D**	**D**						

RHEOLOGY		**BHR**	**AHR**	**AHR**	**AHR**						
Temperature	ºC	**50**	**2**	**20**	**50**	**50**	**50**	**50**	**50**	**50**	**50**
600 rpm	lbs/100ft²	32	76	52	31						
300 rpm	lbs/100ft²	22	48	34	21						
200 rpm	lbs/100ft²	17	37	27	17						
100 rpm	lbs/100ft²	12	25	18	12						
6 rpm	lbs/100ft²	4	7	6	4						
3 rpm	lbs/100ft²	3	6	5	3						
10 second gel	lbs/100ft²		8	6	4						
10 minute gel	lbs/100ft²		11	9	6						
Plastic Viscosity	cP	10	28	18	10	0	0	0	0	0	0
Yield Point	lbs/100ft²	12	20	16	11	0	0	0	0	0	0

FILTRATION - API											
API	ml			5,2							

pH		9,9		8,5							
Specific gravity	sg			1,10							

COMMENTS

385 g basefluid + 4,2 g Luvicap 55w - mixed on Silverson for 10 min - no foam

AHR: Some big air bubbles when mixed on Hamilton, dissapeared quickly.
Rheology: No foam.

Fluid loss was improved.

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DRILLING FLUID FORMULATIONS AND TEST RESULTS

SAMPLE INFO		
REQUEST NO	**Master project Carina Robberstad**	Confidential
FLUID SYSTEM	**Glydril 1,1 SG with 6000ppm Luvicap 55w and 6000ppm Arquad 12-30**	
DESCRIPTION	**WBM**	
TEST DATE	**13.09.12-18.09.12**	
TESTED BY	**Carina Robberstad**	

SAMPLE COMPOSITION												
Sample												
Mixing / Testing date												
Mixing volume			**1000mL**									
Freshwater		g/l	921,5									
KCl	MIN 11-087	g/l	50									
Soda Ash	MIN 08-270	g/l	1									
Polypac ELV	MIN 08-442	g/l	15									
Duotec NS	MIN 11-090	g/l	3									
Glydril MC	MIN 11-099	g/l	20									
Barite (reg)	MIN 12-055	g/l	89,5									
		g/l										
Arquad 12-30		g/l	6									
Luvicap 55w		g/l	6									
		g/l										
		g/l										

AGING CONDITIONS											
Period aged	HOURS		**16**	**16**	**16**						
Temperature	ºC		**100**	**100**	**100**						
Dynamic / Static	D/S		**D**	**D**	**D**						

RHEOLOGY		**BHR**	**AHR**	**AHR**	**AHR**						
Temperature	ºC	**50**	**2**	**20**	**50**	**50**	**50**	**50**	**50**	**50**	**50**
600 rpm	lbs/100ft²	47	76	54	31						
300 rpm	lbs/100ft²	31	48	35	21						
200 rpm	lbs/100ft²	24	37	28	17						
100 rpm	lbs/100ft²	15	24	19	12						
6 rpm	lbs/100ft²	4	7	6	4						
3 rpm	lbs/100ft²	3	6	5	3						
10 second gel	lbs/100ft²		7	6	4						
10 minute gel	lbs/100ft²		10	8	6						
Plastic Viscosity	cP	16	28	19	10	0	0	0	0	0	0
Yield Point	lbs/100ft²	15	20	16	11	0	0	0	0	0	0

FILTRATION - API											
API	ml			5,8							

pH		9,9		8,4							
Specific gravity	sg			1,10							

COMMENTS

385 g basefluid + 2,1 g Luvicap 55w + 2,1 g Arquad 12-30 - mixed on Silverson for 10 min each - no foam - some small air bubbles
Mixed first with surfactant and then with polymer.

50C - Some foaming BHR and AHR at Rheology.
AHR: A lot of foam, over the edge of the mixing cup when mixed on Hamilton, used 5 drops of defoamer.

Very small differences in rheology measurements on BHR 50oC and AHR 2oC samples.
More defoamer neededto be added when mixed on Hamilton Beach AHR.
Some foaming during rheology measurements on BHR and AHR 50oC samples.

DRILLING FLUID FORMULATIONS AND TEST RESULTS

SAMPLE INFO		
REQUEST NO	**Master project Carina Robberstad**	Confidential
FLUID SYSTEM	**Glydril 1,1 SG with 6000ppm Luvicap 55w and 6000ppm SDS**	
DESCRIPTION	**WBM**	
TEST DATE	**13.09.12-18.09.12**	
TESTED BY	**Carina Robberstad**	

SAMPLE COMPOSITION												
Sample												
Mixing / Testing date												
Mixing volume			**1000mL**									
Freshwater		g/l	921,5									
KCl	MIN 11-087	g/l	50									
Soda Ash	MIN 08-270	g/l	1									
Polypac ELV	MIN 08-442	g/l	15									
Duotec NS	MIN 11-090	g/l	3									
Glydril MC	MIN 11-099	g/l	20									
Barite (reg)	MIN 12-055	g/l	89,5									
		g/l										
SDS solution		g/l	15									
Luvicap 55w		g/l	6									
		g/l										
		g/l										

AGING CONDITIONS											
Period aged	HOURS		**16**	**16**	**16**						
Temperature	ºC		**100**	**100**	**100**						
Dynamic / Static	D/S		**D**	**D**	**D**						

RHEOLOGY		**BHR**	**AHR**	**AHR**	**AHR**						
Temperature	ºC	**50**	**2**	**20**	**50**	**50**	**50**	**50**	**50**	**50**	**50**
600 rpm	lbs/100ft²	33	96	67	37						
300 rpm	lbs/100ft²	22	62	43	25						
200 rpm	lbs/100ft²	17	47	34	20						
100 rpm	lbs/100ft²	12	30	22	14						
6 rpm	lbs/100ft²	4	8	7	4						
3 rpm	lbs/100ft²	3	7	6	3						
10 second gel	lbs/100ft²		8	8	4						
10 minute gel	lbs/100ft²		12	10	6						
Plastic Viscosity	cP	11	34	24	12	0	0	0	0	0	0
Yield Point	lbs/100ft²	11	28	19	13	0	0	0	0	0	0

FILTRATION - API											
API	ml			6,0							

pH		9,9		8,5							
Specific gravity	sg			1,10							

COMMENTS

385 g basefluid + 2,1 g Luvicap 55w + 5,25 g SDS - mixed on Silverson for 10 min each - no foam
Mixed first with surfactant and then with polymer.

SDS solution: 20% active (other solutions 50% active) - more diluted/more water in mud(?!)

AHR: Some big air bubbles when mixed on Hamilton, dissapeared quickly, big lumps when taken out of cell, lumps dissapeared with mixing.
50C - Some foaming BHR and AHR at Rheology.

AHR: white particles started separating out quickly, also when performing rheology, dissapeared when mixed on Hamilton Beach again.

Rheology measurements on AHR samples increased slightly.
Some foaming during rheology measurements on BHR 50oC and AHR 50oC samples.

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DRILLING FLUID FORMULATIONS AND TEST RESULTS

SAMPLE INFO		
REQUEST NO	**Master project Carina Robberstad**	Confidential
FLUID SYSTEM	**Glydril 1,1 SG with 6000ppm Luvicap 55w and 6000ppm Imbentin-AG/124S/040**	
DESCRIPTION	**WBM**	
TEST DATE	**25.10.12-26.10.12**	
TESTED BY	**Carina Robberstad**	

SAMPLE COMPOSITION												
Sample												
Mixing / Testing date												
Mixing volume			**1000mL**									
Freshwater		g/l	921,5									
KCl	MIN 11-087	g/l	50									
Soda Ash	MIN 08-270	g/l	1									
Polypac ELV	MIN 08-442	g/l	15									
Duotec NS	MIN 11-090	g/l	3									
Glydril MC	MIN 11-099	g/l	20									
Barite (reg)	MIN 12-055	g/l	89,5									
		g/l										
Imbentin-AG/124S/040		g/l	6									
Luvicap 55w		g/l	6									
		g/l										
		g/l										

AGING CONDITIONS											
Period aged	HOURS		**16**	**16**	**16**						
Temperature	ºC		**100**	**100**	**100**						
Dynamic / Static	D/S		**D**	**D**	**D**						

RHEOLOGY		BHR	AHR	AHR	AHR						
Temperature	ºC	**50**	**2**	**20**	**50**	**50**	**50**	**50**	**50**	**50**	**50**
600 rpm	lbs/100ft²	40	160	66	28						
300 rpm	lbs/100ft²	24	101	44	18						
200 rpm	lbs/100ft²	18	71	34	14						
100 rpm	lbs/100ft²	12	43	23	9						
6 rpm	lbs/100ft²	3	11	8	3						
3 rpm	lbs/100ft²	2	9	6	2						
10 second gel	lbs/100ft²		10	7	3						
10 minute gel	lbs/100ft²		14	9	3						
Plastic Viscosity	cP	16	59	22	10	0	0	0	0	0	0
Yield Point	lbs/100ft²	8	42	22	8	0	0	0	0	0	0

FILTRATION - API											
API	ml			5,0							

pH		9,8		8,2							
Specific gravity	sg			1,10							

COMMENTS

385 g basefluid + 2,1 g Luvicap 55w + 2,1 g Imbentin-AG/124S/040 - mixed on Silverson for 10 min each - no foam
Mixed first with surfactant and then with polymer.

Foaming AHR when mixed on Hamilton Beach, 8 drops of defoamer added.
No foam during Rheology at 20 and 50oC.
Very viscous fluid at Rheology at 2oC.

Rheology measurements on BHR 50oC sample increased slighlty at the high-end, and decreased slightly at the low-end.
Rheology measurements on AHR 50oC sample decreased slightly and the 10min gel was half of that of the base fluid.
Rheology measurements on AHR 20oC sample increased somewhat.
Rheology measurements on AHR 2oC sample was twice as high as that of the base fluid at the high-end and also slightly higher at the low-end.

Smells and stings in eyes, throat and nose. Especially AHR sample.

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DRILLING FLUID FORMULATIONS AND TEST RESULTS

SAMPLE INFO		
REQUEST NO	**Master project Carina Robberstad**	Confidential
FLUID SYSTEM	**Glydril 1,1 SG with 6000ppm Luvicap 55w and 6000ppm Cdld-151**	
DESCRIPTION	**WBM**	
TEST DATE	**25.10.12-26.10.12**	
TESTED BY	**Carina Robberstad**	

SAMPLE COMPOSITION												
Sample												
Mixing / Testing date												
Mixing volume			**1000mL**									
Freshwater		g/l	921,5									
KCl	MIN 11-087	g/l	50									
Soda Ash	MIN 08-270	g/l	1									
Polypac ELV	MIN 08-442	g/l	15									
Duotec NS	MIN 11-090	g/l	3									
Glydril MC	MIN 11-099	g/l	20									
Barite (reg)	MIN 12-055	g/l	89,5									
		g/l										
Cdld-151		g/l	6									
Luvicap 55w		g/l	6									
		g/l										
		g/l										

AGING CONDITIONS											
Period aged	HOURS		**16**	**16**	**16**						
Temperature	ºC		**100**	**100**	**100**						
Dynamic / Static	D/S		**D**	**D**	**D**						

RHEOLOGY		**BHR**	**AHR**	**AHR**	**AHR**						
Temperature	ºC	**50**	**2**	**20**	**50**	**50**	**50**	**50**	**50**	**50**	**50**
600 rpm	lbs/100ft²	34	79	54	32						
300 rpm	lbs/100ft²	23	50	36	22						
200 rpm	lbs/100ft²	18	39	29	18						
100 rpm	lbs/100ft²	13	26	20	13						
6 rpm	lbs/100ft²	4	8	7	5						
3 rpm	lbs/100ft²	3	7	6	4						
10 second gel	lbs/100ft²		7	7	6						
10 minute gel	lbs/100ft²		12	9	7						
Plastic Viscosity	cP	11	29	18	10	0	0	0	0	0	0
Yield Point	lbs/100ft²	12	21	18	12	0	0	0	0	0	0

FILTRATION - API											
API	ml			5,6							

pH		9,3		6,2							
Specific gravity	sg			1,10							

COMMENTS

385 g basefluid + 2,1 g Luvicap 55w + 2,1 g Cdld-151 - mixed on Silverson for 10 min each - no foam
Mixed first with AA and then with polymer.
No foaming AHR on Hamilton Beach.
No foam during Rheology.

Rheology increased slightly at AHR low-end measurements.
AHR sample had a much lower pH-value compared to the base fluid - acidic.

Smells and stings in eyes, throat and nose. Especially AHR sample.

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DRILLING FLUID FORMULATIONS AND TEST RESULTS

SAMPLE INFO		
REQUEST NO	**Master project Carina Robberstad**	Confidential
FLUID SYSTEM	**Glydril 1,1 SG with 6000ppm Luvicap 55w and 6000ppm Cdld-445**	
DESCRIPTION	**WBM**	
TEST DATE	**25.10.12-26.10.12**	
TESTED BY	**Carina Robberstad**	

SAMPLE COMPOSITION												
Sample												
Mixing / Testing date												
Mixing volume			**1000mL**									
Freshwater		g/l	921,5									
KCl	MIN 11-087	g/l	50									
Soda Ash	MIN 08-270	g/l	1									
Polypac ELV	MIN 08-442	g/l	15									
Duotec NS	MIN 11-090	g/l	3									
Glydril MC	MIN 11-099	g/l	20									
Barite (reg)	MIN 12-055	g/l	89,5									
		g/l										
Cdld-445		g/l	6									
Luvicap 55w		g/l	6									
		g/l										
		g/l										

AGING CONDITIONS											
Period aged	HOURS		**16**	**16**	**16**						
Temperature	ºC		**100**	**100**	**100**						
Dynamic / Static	D/S		**D**	**D**	**D**						

RHEOLOGY		BHR	AHR	AHR	AHR						
Temperature	ºC	**50**	**2**	**20**	**50**	**50**	**50**	**50**	**50**	**50**	**50**
600 rpm	lbs/100ft²	34	79	53	32						
300 rpm	lbs/100ft²	23	50	36	22						
200 rpm	lbs/100ft²	18	39	29	18						
100 rpm	lbs/100ft²	13	26	20	13						
6 rpm	lbs/100ft²	4	8	7	5						
3 rpm	lbs/100ft²	3	7	6	4						
10 second gel	lbs/100ft²		8	7	5						
10 minute gel	lbs/100ft²		11	9	6						
Plastic Viscosity	cP	11	29	17	10	0	0	0	0	0	0
Yield Point	lbs/100ft²	12	21	19	12	0	0	0	0	0	0

FILTRATION - API											
API	ml			5,0							

pH		9,4		6,3							
Specific gravity	sg			1,10							

COMMENTS

385 g basefluid + 2,1 g Luvicap 55w + 2,1 g Cdld-445 - mixed on Silverson for 10 min each - no foam
Mixed first with AA and then with polymer.
No foaming AHR on Hamilton Beach.
No foam during Rheology.

Fluid loss was improved.
Rheology increased slightly at AHR low-end measurements.

AHR sample had a much lower pH-value compared to the base-fluid - acidic.

Smells and stings in eyes, nose and throat. Especially AHR sample.