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Demulsification of Highly Stable Water-in-Oil Emulsions

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ABSTRACT

Emulsification and subsequent separation characteristics of water-in-crude-oil emulsions are studied using crude oil from the Norsk Hydro, Norway. In particular, the effects of high pressure, carbon dioxide gas, and electric field on the de-emulsification of water-in-crude-oil emulsions are considered. Emulsions of varying degree of stability were produced, and their natural separation rate under gravity was recorded. Emulsions of known separation characteristics were prepared and subjected to separation tests with electrostatic field, surfactant de-emulsifiers, and high pressure in the absence or presence of carbon dioxide. Purpose-built

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equipment was used in the electric field and pressure experiments. The different levels of emulsion stability were found to depend on the composition of the oil sample as well as the processing conditions. The heavy fractions formed emulsions much more readily and were significantly more stable. The separation enhancement was achieved through the application of high pressures to the emulsions. But the high pressure was not sufficient to have any significant impact when the emulsion was highly stable. The addition of carbon dioxide from a 50-bar supply did not have any effect, adverse or otherwise, on this improvement. Tests with application of a high-voltage electrostatic field on the oil revealed that lower-stability emulsions at least are susceptible to this method of separation. A number of chemicals were also used as chemical de-emulsifiers and were found to have no effect on enhancing the separation. These studies were conducted in order to provide the background for the intensification of the oil/water separation technique developed by the authors.

INTRODUCTION

Water-in-crude-oil emulsions are dispersions of fine water droplets in crude oil. The dispersed phase droplets are prevented from coalescing, and therefore from separating, by an adsorbed layer of surface-active species that are naturally available in crude oil. These emulsions are commonly encountered in crude oil production as well as processing. They are undesirable as they not only cause serious processing problems but also lead to significant cost increases (transportation difficulties and equipment decay as a result of corrosion and scale problems). Thus, prior to downstream oil processing, it is necessary to remove the dispersed water, which most of the time has high level of salt and other impurities, by suitable processes. The first step is to break down the emulsion to its main constituents (water and oil).

It is expected that the dispersed-phase particle size distribution will be dictated by the past flow history as well as by the surface activity of the indigenous surfactants in the oil. Although the flow effects in emulsions observed by Akay[1,2] can be useful in breaking down emulsions formed during the production and transportation of crude oil, to break water-in-oil emulsions is more art than science since the mechanism by which these emulsions are stabilized is not well understood.[3] This is especially true in the case of the crude oil emulsions, as the existing crude oils display great differences in their characteristics, a common behavior in natural feed stocks. Therefore, a method that is successful in treating emulsions of a particular crude oil may not be successful in treating emulsions of other types of crude oils. What is even worse is that the oil-extraction process itself may actually stabilize the emulsion. But, whatever method is being used, ideally, oil–water separation should be as close to the source of production as possible. This makes the down-hole or sub-sea separations preferable. Such a process has to be compact, robust, and simple. The pressures involved will be very high (up to 5000 psi) and the temperature can reach 60–70°C. It is therefore necessary to understand the behavior of oil–water systems under these prevailing conditions. Central to this understanding is the identification of the surface-active materials in the crude oil and their behavior at the pressures and temperatures mentioned. Such studies are extremely rare. Studies done under atmospheric pressure indicate that addition of synthetic surfactants to oil–water systems may lead to stabilization as well as to destabilization of the emulsions formed, depending on the characteristics of the oil, mainly the type of indigenous surface-active species. The presence of other components, such as gases and colloidal particles—will also complicate the kinetics of oil–water separation. Thus it is very important that oil be characterized by identifying the indigenous surface-active components as well as by determining its other properties such as viscosity, density, and interfacial tension before choosing a suitable emulsion treatment method. Depending on the relative phase volumes of the oil and water phases and the viscosity of the oil phase, the oil–water systems exist either as oil or water continuous emulsions.

The objective of the study is to investigate the kinetics of stable oil–water separation in oil continuous emulsions at high pressures as a function of the characteristics of oil and aqueous phases, pressure, and electric field.

Effect of Pressure

The effect of pressure on the formation and stabilization of water-in-crude-oil natural emulsions has not been investigated. Clarke[4] suggested that crude oils with good water-retention (i.e., emulsion-forming) capability would probably contain asphaltene and wax sols as well as oil soluble surfactants such as C_0–C_3 alkylphenols. Dale[5] in a study on the distributions of alkylphenols and aromatic hydrocarbons in crude oils and coexisting waters reported that the partition behavior of alkylphenols in a crude oil and water system was mainly influenced by temperature and salinity and only slightly by pressure. If the partitioning of these organic solutes in coexisting oil and water phases is considered to be the major cause for the formation of emulsions and their stabilization, then it may be concluded that pressure will have a minimal effect on water-in-crude-oil emulsions.

It is been suggested in a study on pressure-induced structural changes in microemulsion droplets stabilized by sodium dioctyl sulfosuccinate (Aerosol-OT, AOT) by Steyler et al.[6] that the scope for pressure-induced structural changes in water dispersions would be small unless the system is close to a phase boundary or, as in the case of certain surfactants in aqueous solution, susceptible to micellar shape changes. But Sjoblom et al.[7] suggested that the parallel between microemulsions and true emulsions is not completely valid, as the former represents thermodynamically stable emulsions whereas the later is kinetically stabilized and in a dispersed state. Moreover, the droplet sizes as well as interfacial conditions would also deviate. Thus it seems that findings reported on the effect of the pressure on the microemulsions will not be directly relevant to crude oil emulsions. There appears to be a large number of studies on the behavior of surfactants in supercritical or near-supercritical fluid (mainly CO_2)–water systems (mainly microemulsions).[8–12] These may be helpful to a certain extent in the understanding of the behavior of surfactants under high pressures in true emulsions. If a parallel between emulsions of supercritical fluids and crude oil emulsions can be validated, the results of these studies can also be used in predicting the behavior of the crude oil emulsions under high pressure.

Another field in which the effect of high pressure on the structural changes of the species showing surfactant characteristics (mainly proteins) has been investigated is the food processing and drug delivery formulations.[13–16] But the pressures involved in these applications are in the ultra-high-pressure range (up to 1000 MPa), which is well in excess of those likely to occur in crude oil productions (up to 20 MPa). At relatively low pressures (20 MPa) the pressure-attributed effects in food emulsions appear to be insignificant.

Therefore, it appears to be necessary to carry out a fundamental investigation on the effect of the pressure on true crude oil emulsions. Given the broad variation in the characteristics of the existing crude oils, the result obtained for a particular type of crude oil may not be valid for other certain types of crude oils. This points out the importance of the evaluation of the effects of the crude oil characteristics on the emulsion formation and stabilization and the possible influence of the pressure on them.

Effect of Oil Phase Characteristics

It is well known that the characteristics of a given crude oil play an important role not only in the formation of stable emulsions but also in deciding what method to use to destabilize these emulsions.[17–25] It seems that surface-active chemical content of the oil, especially the amount of asphaltenes and resins, is crucially important. The physicochemical properties, such as viscosity, density, surface tension, and interfacial tension, also appear to be equally important. But little known is how the influence of physicochemical properties on the emulsion stability will be altered by the chemical content and vice versa. Even less known is how all these properties will change under downhole (high-pressure and -temperature) conditions, and therefore, how the emulsion stability will be influenced. Thus it once more becomes apparent that there is a need for fundamental research to investigate the effect of the pressure on the characteristics of crude oils and their emulsions.

Effect of Aqueous Phase Characteristics

Significant changes in interfacial film behavior, therefore in emulsion stability, often occur due to aqueous phase chemical content differences, mainly those of salts. Jones et al.[17] reported that specific ion effects may also occur. They showed that for a typical crude oil (Murban), Mg^{2+} ions lead to an increased relaxation of the film formed and a decrease in the resistance to compression compared to distilled water. On the other hand for Ca^{2+} the film build up rate was observed to be slower than for distilled water, and eventually highly stable emulsions were produced by Ca^{2+}. They also showed that incompressible nonrelaxing films resulted when water contained a high Ca^{2+} / low Mg^{2+} ion ratio irrespective of total salinity.

The effect of metal ions on the hardness/compressibility of surfactants has been studied by the present authors[26–28] using dead-end or crossflow filtration and proton relaxation NMR methods. It was shown that different ions acting on the same surfactant could result in "harder" or "softer" surfactant phase as determined by T_2 relaxation time.

Effect of Electric Field

High-electric-field–induced coalescence of dispersed water droplets is a well known method to break down emulsions and to cause water–oil separation. The first commercial use of the high-electric-field coalescers took place in 1909 shortly after the pioneering work by Cotrell in 1907.[29] Since then significant amount of improvement has been made as a result of a great deal of effort spent on the design of new coalescers, with the aim of finding the optimum conditions for the best water–oil separation with respect to the electric field (intensity and the type and the frequency).[30–58] It appears that the same technique can also be used in emulsification by enhancing the efficiency of the dispersion (the breakup) of the water droplets under external electric fields. A group of researchers in Korean Advanced Institute of Science and Technology showed that small subdrops were formed as a result of the breakup of the larger parent drops under electric fields.[59] This indicates that when applying electric-field-induced demulsification technique, one must exercise care in order to not further stabilize the emulsion by the electric-field-induced droplet size reductions.

As mentioned above, numerous studies have been carried out on electric-field-induced demulsification. But much of these works have concentrated on model emulsions and fewer on the crude oil emulsions. To the knowledge of the present investigators, there appears to be no study carried out on the effects of high pressure on the high-electric-field dewatering of crude oils. The mechanism and the theory of the technique under the atmospheric pressure have been well investigated; see, for example, Gang et al.[60]

EXPERIMENTAL DETAILS

Emulsion Preparations

Preliminary emulsions were prepared in graduated glass test tubes of 25-ml volume by using a vortex generator in order to determine the stability of the emulsions with various dispersed phase volumes. In these tests the type and the concentration of synthetic surfactants, and composition of water and oil phases, were varied. The synthetic surfactants tested were nonionics sorbitan monooleate (Span 80) and sorbitan monolaurate (Span 20) and anionic surfactant sodium dioctyl sulfosuccinate (Aerosol-OT, AOT).

Emulsions used in the separation test were prepared in a stainless steel laboratory-scale impeller mixer. The mixer had a diameter of 12 cm and had an approximate nominal volume of 550 ml. An integral heating/cooling jacket was available. The stirrer was powered by an electric motor allowing rotation speeds over a range of 200–600 rpm and was attached to a double impeller comprising two 2-bladed simple paddles inclined at approximately 45 degrees. The paddles were 100 mm in length and at 90 degrees to each other. The whole unit was mounted onto a frame to provide access above and below as well as stability.

Emulsions were produced with a volume of 250 ml. These consisted of varying ratios of oil and water and were run at a number of different impeller speeds. The oil phase (as received from Norsk Hydro) and aqueous phase, containing $NaCl_2$: 28.1 g/L; $CaCl_22H_2O$: 0.6 g/L; $MgCl_26H_2O$: 5.0 g/L; and with a density of 1.021 g/ml were added to vessel together. The mixing time was also altered significantly in order to produce emulsions of different levels of stability. After the preparation, the emulsion (at 20°C) was fed into the separation cell using a peristaltic pump, as shown in Fig. 1.

Water/Oil Separation

A custom-built electric field pressure vessel was employed for water/oil separation from the emulsions prepared as previously described. The system

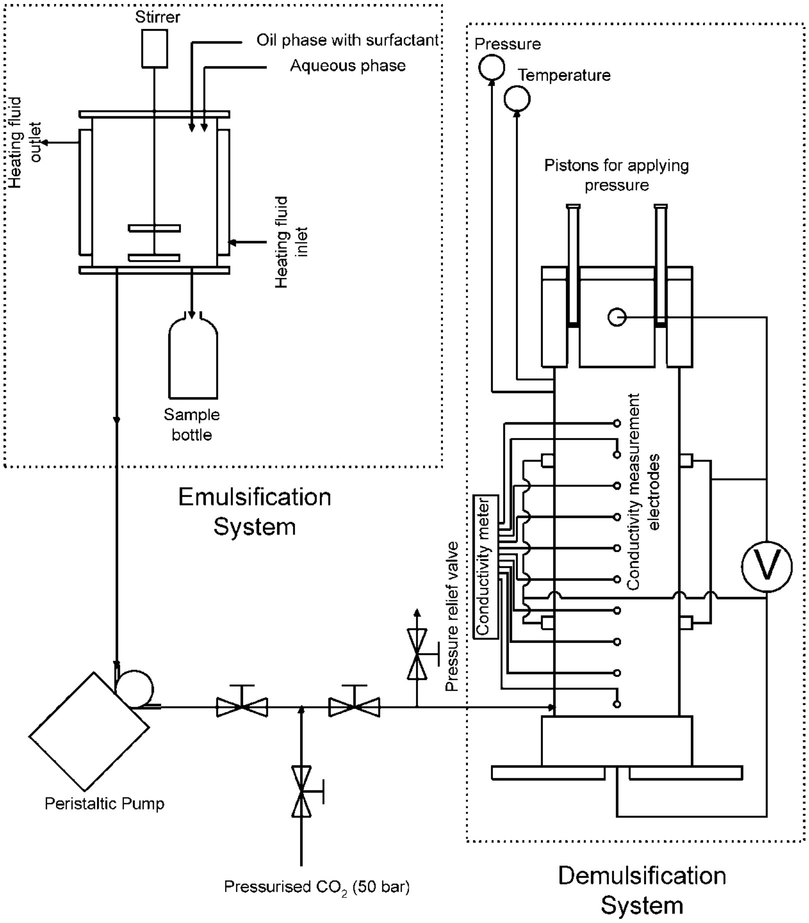

Figure 1. Schematic display of the experimental system.

was designed to allow the investigation of oil-water and other liquids under pressure and electric field. Figure 2 shows a photograph of the system.

The system comprises a pressure vessel of cylindrical outer shape, electric field electrodes, and conductivity-measurement electrodes. The pressure vessel has a vertical axis and is freestanding. It incorporates a filling line, two hand-driven pistons to provide pressures up to 35 MPa (5000 psi), and temperature and pressure sensors. The filling line comprises a valve for emulsion feed, a valve for carbon dioxide supply, and a pressure-relief valve.

The vessel consists of three pieces: (i) a piston block acting as a cap on the top, (ii) a hollow cylinder with PTFE inserts forming a rectangular channel with conductivity and high-electric-field electrodes, and (iii) a base block at the bottom. The top cap, which houses the hand-driven pistons, is fixed onto the unit via four large screws. Their main function is to hold the cap in position so that the pistons are properly aligned. When the pistons are screwed down and inducing high pressures they also (inherently) secure the top cap to the unit. This is a safety feature and ensures that at no stage are there high pressures and an unsecure lid.

The electric field electrodes comprise one pair vertical-field phosphor-bronze electrodes and one pair horizontal-field phosphor-bronze electrodes. The vertical field electrodes with 40 mm × 40 mm size are located in the piston

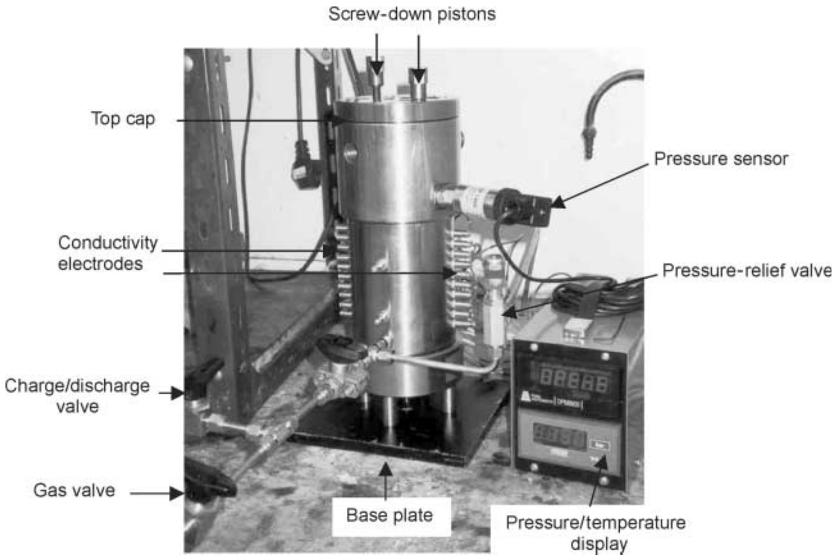

Figure 2. Photograph of high-pressure de-emulsification cell.

block at the top of the vessel and in the base at the bottom of the vessel. The horizontal field electrodes are located on either side of the central piece of the vessel. They have been designed to have the same area as the vertical field electrodes and measure 110 mm × 14.5 mm with semicircular ends. There are ten pairs of resistivity/conductivity-measuring electrodes of 38 mm × 5 mm size with semicircular ends equally spaced up opposite sides of the cavity from the bottom of the central piece with 6 mm distance between them with external connections. These are used to determine the nature of the liquid phase (oil or water) at different heights due to their vastly different readings, water being a much better electrical conductor. The distance between the flat vertical high-electric-field electrodes and the first (at the bottom) or the last (on the top) conductivity electrodes is 12 mm.

The electrode seals need to be able to withstand the very high pressures. The seals are constructed using an O-ring, a backup ring, a sealing collar, and a cap ring. The external connection is made via the electrode stud, which must not be overtightened or the integrity of the seal will be lost.

Connections are made to the conductivity/resistivity electrodes by ten pairs of wires that run into a junction box. Attached to this is a conductivity meter, allowing individual measurement of all the electrode pairs. During experiments the unit was often left at high pressure for several days at a time. For safety reasons it was isolated in a closed-fume cupboard.

Once the emulsion was fed into the vessel, all the trapped air was removed by repetitive pressurizing and depressurizing by the pistons. The high pressure is induced in the unit via screwing down the hand-driven pistons until the required pressure is reached as indicated on the pressure sensor readout. The internals of the unit are constructed with PTFE, and over time at high pressure, creep occurs causing the pressure to drop. This is overcome through further tightening of the pistons. After topping up the vessel with the emulsion from the piston holes, CO_2 at 50 bar, when used, was fed into the vessel and line was kept open for an hour. Following this initial pressurization with CO_2, further pressure was applied (up to a total pressure of 200 bar) by screwing down the pistons. The emulsion was kept under this pressure and laboratory temperature ($18 \pm 1°C$) for a predetermined period of time. The readings from the conductivity electrodes were recorded by using a conductivity meter at fixed time intervals for the observation of the phase separation.

In this study, the effect of electric field was investigated at atmospheric pressure using a Perspex electric field cell, which allowed the separation to be observed visually. A high-voltage (up to 30-kV) DC electric field could be applied to this—as shown in Fig. 3. The cell comprises two Perspex blocks held together with six wing nut bolts; a hollow central cavity

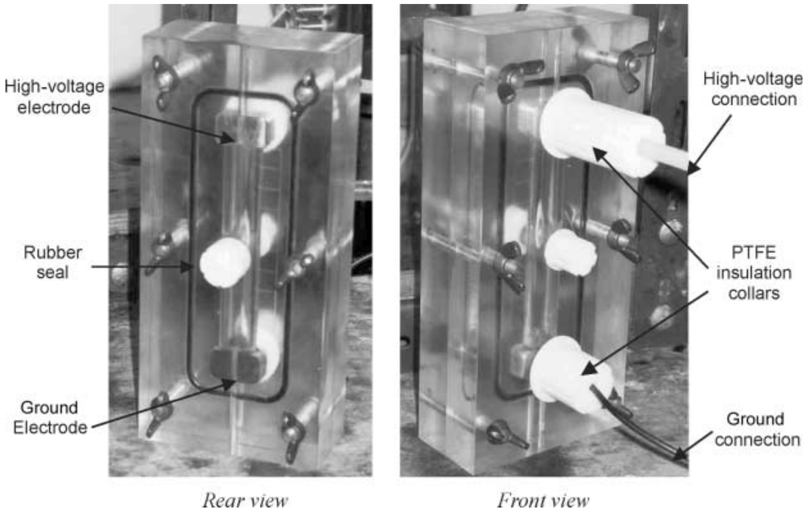

Figure 3. Photograph of Perspex electric field cell.

providing approximately 30 ml volume; two stainless steel electrodes, one insulated, providing a vertical electrical field; PTFE insulation covers at the electrode connections, a rubber seal between the blocks; top vent open to atmospheric pressure; side charging port; and graduated volume measurements.

The emulsions may be injected to the cell via the side charging port which is closed when full. The bottom electrode has been fully insulated using shellac and liberal amounts of vacuum grease. The top electrode is connected to the high positve potential and the bottom electrode is connected to ground.

When the voltage is applied it is done so by gradually increasing from zero. An ammeter is present on the electrical equipment scaled to 15 mA. If it reaches this maximum the system is designed to short out for safety reasons. Indication that it is about to short out is obvious by minor fluctucations on the ammeter. In the case of normal operation there should be no current. At such high voltages arcing may occur and result in damage to the unit as the electrical energy converts to heat and light. Oil is of course a flammable liquid, and it is desirable to avoid any source of ignition. Further to this, when the unit has been turned off it is left for ten minutes before any of the equipment is handled to ensure there is no residual electric charge present.

RESULTS

Emulsification

As knowledge of emulsification characteristics of crude oils is important not only for the field operations but also downstream crude oil processing, a significant amount of emulsification tests were carried out with different crude oil samples provided by Norsk Hydro, Norway. The aim of these tests was to obtain a model emulsion that would remain stable for 14 days (i.e., 90% separation) so that any effects due to the external factors (high pressure, electric field, and additives) could be evaluated unambiguously. Moreover, the knowledge gathered can also be used in future experimental work as well as in practical crude oil applications.

Some preliminary test tube emulsification tests were carried out for determining conditions for a stable emulsion using Norsk-Hydro Oil A. The results are summarized in Table 1. When no surfactant was used, the oil and water mixtures separated to individual phases immediately following the initial mixing. Remixing the tube contents repeatedly on successive days lead to the formation of some cellular water pockets separated by thin oil films. The size of these cells became smaller with time. After a month they reduced to submillimeter in size. This indicated that the oil contained some surface-active material, which adsorbed very slowly to the oil-water interface as the time passed. Similar results have been reported by Jones et al.[17] They have found that interfacial contact time for most oil-water systems significantly affects the emulsion stability and claimed that emulsions prepared in the laboratory from freshly contacted oil and water phases would not give a good guide to stability of the emulsions encountered in crude oil production and processing systems. No water-phase separation occurred from the emulsions prepared with added surfactants in the oil phase as the time passed. Excess oil phase separated at the top of the tubes of which quantity decreased with increasing surfactant concentration. The emulsion below the separated oil layer was water-in-oil type in which the internal aqueous phase volume increased with time as more oil separated at the top.

Some emulsions with initial 125-ml aqueous phase and 125-ml oil phase have been prepared using the mixer described in the experimental section. The type of synthetic surfactants as well as their concentrations and the mixing time varied during these tests. The results obtained are summarized in Table 2. The behavior observed was generally similar to that in test tube experiments. Aging of these relatively large volume emulsions also lead to no aqueous phase separation.

Table 1. Some typical results of the test tube emulsification tests with Norsk-Hydro Oil A.

Initial phase volumes			First phase volumes (ml)			Last phase volumes (ml)		
$V_{aq.}$ (ml)	V_{oil} (ml)	Surfactant (concentration)	$V_{aq.}$	$V_{em.}$	V_{oil}	$V_{aq.}$	$V_{em.}$	V_{oil}
5.0	5.0	—	5.0	0	5.0	0	5.5	4.5
2.5	7.5	—	2.5	0	7.5	0	3.0	7.0
1.0	9.0	—	1.0	0	9.0	0	1.5	8.5
0.5	9.5	—	0.5	0	9.5	0	1.0	9.0
7.5	2.5	Span 80 (5%)	0	9.8	0.2	0	10	0
5.0	5.0	Span 80 (5%)	0	9.0	1.0	0	9.5	0.5
2.5	7.5	Span 80 (5%)	0	7.5	2.5	0	8.5	1.5
1.0	9.0	Span 80 (5%)	0	3.5	6.5	0	8.0	2.0
0.5	9.5	Span 80 (5%)	0	1.0	9.0	0	8.0	2.0
5.0	5.0	Span 20 (5%)	0	9.8	0.2	0	9.8	0.2
2.5	7.5	Span 20 (5%)	0	9.0	1.0	0	7.0	3.0
1.0	9.0	Span 20 (5%)	0	3.5	6.5	0	4.0	6.0
7.5	2.5	Span 80 (2%)	0	9.0	1.0	0	9.8	0.2
5.0	5.0	Span 80 (2%)	0	7.0	3.0	0	8.5	1.5
2.5	7.5	Span 80 (2%)	0	4.5	5.5	0	5.0	5.0
1.0	9.0	Span 80 (2%)	0	2.0	8.0	0	2.5	7.5
5.0	5.0	AOT (1%)	0	6.0	4.0	0	6.0	4.0
5.0	5.0	Span 20 (0.5%)	0	6.0	4.0	0	7.0	3.0
5.0	5.0	Span 20 (0.5%)	0	6.0	4.0	0	7.0	3.0
5.0	5.0	Span 20 (0.25%)	0	6.0	4.0	0	6.0	4.0
5.0	5.0	Span 20 (0.125%)	4.5	1.0	4.5	4.5	1.0	4.5
5.0	5.0	Span 20 (0.0625%)	5.0	0.0	5.0	5.0	0	5.0
5.0	5.0	Span 20 (0.0625%)	5.0	0.0	5.0	5.0	0	5.0

Effect of colloidal particles on the emulsion stabilization was investigated by the addition of hydrophobic (particle size: 16 nm) or hydrophilic (particle size: 7 nm) silica particles. These were supplied by Degusse and coded as Aerosil R812 or Aerosil 380, respectively. The aim of these tests was to simulate the influence of fine solid particles available in produced crude oils. In these tests the silica concentration was 0.5% by weight in individual phases (oil in the case of the hydrophobic one and aqueous in the case of the hydrophilic one). The results obtained are also given in Table 2. It was observed that hydrophilic silica had no emulsion stabilization effect, while

Table 2. Some typical results of mixing tank emulsification tests with Norsk-Hydro Oil A.

Emulsion preparation details				Emulsion properties			
$V_{aq.}$ (ml)	V_{oil} (ml)	Surfactant (concentration)	Mixing details (rpm, min.)	$V_{aq.}$ (ml)	$V_{em.}$ (ml)	V_{oil} (ml)	Conductivity (μS)
125	125	Span 20 (5%)	600, 150	0	225	25	1.3
125	125	Span 20 (5%)	600, 180	0	225	25	1.3
125	125	Span 80 (5%)	600, 30	0	200	50	1.4
125	125	Aerosil R812 (0.5%)	600, 120	80	50	120	—
125	125	Span 80 (2%), Aerosil R812 (0.5%)	600, 30	0	200	50	1.0
125	125	Aerosil 350 (0.5%)	600, 120	125	0	125	—
125	125	Span 80 (2%), Aerosil 350 (0.5%)	600, 30	0	200	50	1.1
125	125	Span 80 (1%)	600, 30	0	200	50	0.7
125	125	Span 20 (1%)	600, 30	0	200	50	2.2
125	125	Span 20 (0.5%)	600, 30	0	160	90	20

the hydrophobic one produced a coarse emulsion of approximately 20% of the total volume.

Further emulsification tests were carried out using another oil, Norsk-Hydro Oil B. Stable emulsions could be obtained with this oil without any surfactant addition, indicating high content of indigenous surface-active components in this type of oil. The results showed that the emulsification and emulsion characteristics are strongly dependent on the oil composition and therefore, for the repeatability of the experiments, the history of the oil must be known. The fractionation of the crude oil during storage must be overcome in order to obtain repeatable results.

The phase volume of water that could be emulsified to obtain a water-in-crude-oil emulsion was strongly dependent on the type of the surface-active material present as characterized by hydrophilic–lipophilic balance (HLB), as well as the electrolyte concentration.[1,2,61] These results indicate that the HLB of the indigenous surfactants is in the midrange, rather than low HLB range used in the preparation of the high-internal-phase emulsions. It is therefore important to have an assessment of the inherent surface activity in the oil. In oil production this is useful, since the amount of water extracted from a well at any one point varies, the likelihood of emulsions forming may be predicted. This has applications in the oil-processing industry as well as production since emulsions are sometimes formed deliberately in some applications. The results determined the maximum amount of water that, for example, may be used to dissolve the salts in the oil, ensuring an emulsion is not formed. Also, to some extent, the long-term characteristics of the emulsions have been investigated, with the results of their stability or separation rate over several months assessed. Even after 12 months, some of the emulsions seemed to remain stable. Investigations into droplet size and other such evaluative methods will be performed in a future work.

De-emulsification

Effects of high pressure, carbon dioxide gas, and electric field on de-emulsification and water/oil separation characteristics of the emulsions formed without additional surfactant by Norsk-Hydro Oil B were investigated. Results obtained are presented and discussed in the following sections.

Effect of Pressure on Separation

In order to obtain quantitative data concerning the effect of pressure on separation, several water-in-oil emulsions (50–50 water/oil) were prepared at 200 rpm impeller speed and 2 minutes of mixing time. Half of the sample was used for the control experiment at ambient pressure and the other half was pressurized (200 barg) for various time spans. Effects of pressure on the separation were observed using the conductivity electrodes whilst simultaneously observing a control sample of an identical emulsion at atmospheric pressure. The procedure was as follows: (1) Two identical 250-ml solutions (emulsions) of water/oil were made up. (2) One was left to stand as usual, and the other was charged to the high-pressure vessel. (3) Conductivity readings were taken at 0 barg. (4) The pressure was raised to 100 barg, and the conductivity readings were taken again. (5) The pressure was raised to 200 barg, and the conductivity readings were taken again. (6) The vessel was left at 200 barg for several days, with conductivity readings taken again at suitable intervals and recorded.

Figure 4 illustrates the conductivity distribution in the emulsion during storage under pressure. In this particular case, the emulsion contains 30% water and 70% crude oil. The left side of the graph represents the top of the pressure cell, while right side represents the bottom of the cell. The conductivity measurements are used to determine the location of the oil-water interface within an accuracy of 1 cm. As seen in Fig. 4, initially the conductivity recordings are very low as the emulsion is oil continuous.

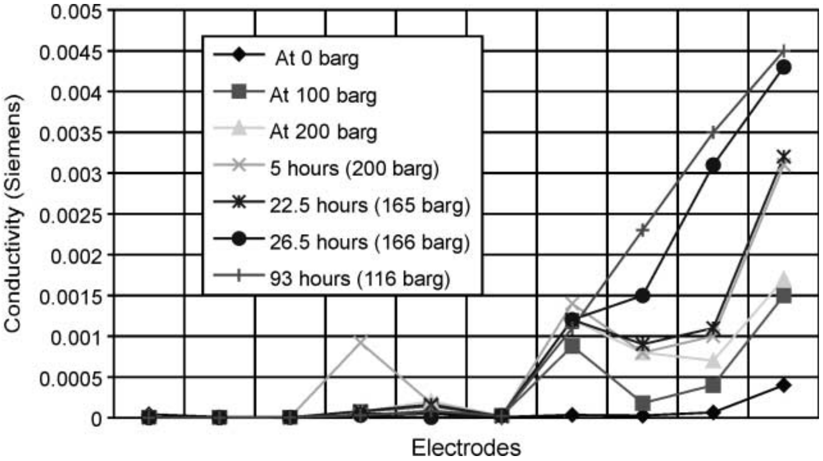

Figure 4. Conductivity readings of the electrodes under different experimental conditions.

When the separation takes place, the conductivity at the bottom of the pressure cell increases. At the electrode locations 4–6 (location 1 represents the top electrode and location 10 represents the bottom of the electrode), when a single-phase liquid is present, the conductivity measurements yield higher values. This is probably due to the electric field effect. However, as seen from Fig. 4, conductivity measurements are high at the bottom electrodes as a result of oil-water separation. One can obtain the oil-water interface by assuming a mean conductivity level below which no separation is present.

Due to the presence of large numbers of seals for the conductivity measurements, it is difficult to maintain the initial pressure at 200 bar. It is therefore necessary to increase the pressure manually every 12 hours. However, due to the creep of the PTFE seals, the rate of pressure decay can be unacceptably fast if the cell is used continuously for a number of weeks. Furthermore, seals of the conductivity electrodes need to be dried since small amount of surface water on the seals can cause short circuiting thus resulting in large errors.

The examination of Fig. 4 indicate that, at time t = 0 when the pressure is increased to 100 barg, there is an overall increase in the conductivity measured by the bottom electrode, clearly showing that the water has, to some extent, become present. A further increase to 200 barg resulted in increasing conductivity that is not a result of phase disengagement (oil-water separation). If the pressure is reduced to atmospheric pressure, conductivity readings also go back to their original value, indicating that there is no permanent phase separation.

After waiting for a set length of time at a given pressure, the cell content at the end of each de-emulsification test was discharged from the pressure cell and the volume of the aqueous phase was measured to calculate the percent separation. Some typical results are shown in Fig. 5. It can clearly be seen from Fig. 5 that the rate of separation increases significantly by increasing the pressure to 200 bar.

Some experiments were carried out at high pressure with carbon dioxide injected into the emulsion at 50 barg. The injection of carbon dioxide into the emulsion was conducted by connecting the high-pressure cell inlet to a gas supply at 50 barg and waiting for an hour. Subsequently, the gas supply was disconnected and the cell was pressurized manually. This experiment was designed to see if the organic gases often found in oil wells (such as methane) have any effect on oil-water separation. Once again the vessel was emptied at each testing point and the amount of water separated observed visually. Some typical results are also presented in Fig. 5. It can be seen that the presence of carbon dioxide does not significantly affect the rate of separation at 200 barg.

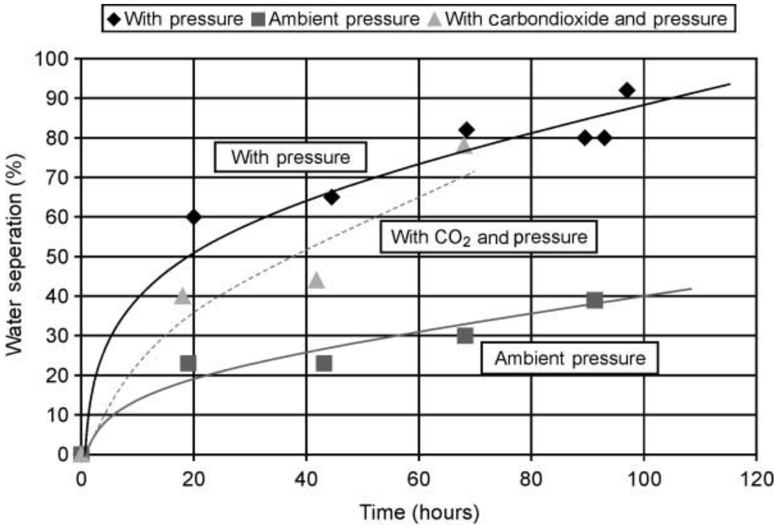

Figure 5. Variation of water separation with time under various conditions. The water-in-oil emulsion contains 50% water. Mixing time = 2 min., impeller speed = 200 rpm.

It was also observed that even when there was no oil/water separation, high pressure resulted in increased conductivity. This probably was a clue that the pressure accelerated the separation process. However, if the emulsion is highly stable (for months), the effect of pressure could not be determined due to the very long periods required for separation.

Effect of Electrical Field on Separation

Some de-emulsification tests under high-voltage electric field and ambient pressure were carried out to investigate the effect of electric field on separation. The results showed that electric field could help separation with varying degrees of success. Less-stable emulsions could be separated with relative ease. However, when a more-stable (emulsion stable for more than 4 weeks) sample was used, the separation achievable in the experiment time of 20 minutes was minimal, although some coagulation of water was observed. Since both electric field and pressure enhance separation, it is likely that their combination will further accelerate the separation. Although the high-pressure cell had the electric field application facility, it was not used in the present experiments.

Effect of Chemical De-emulsifiers on Separation

Effect of some chemical de-emulsifiers on the separation was also investigated. This experimentation served to eliminate several chemicals and types of chemicals as potential de-emulsifiers, at least in the applied concentrations. These de-emulsifiers were hydrophobically modified water-soluble polymers (HMWSPs). These surface-active materials have both stabilization and de-stabilization characteristics depending on their concentration as well as the chemistry of the oil phase, including the molecular weight of both the oil and the HMWSP.[61–66] The amount of HMWSP added to the emulsion represented 0.25% or 0.5% or 1% of the emulsion. At these concentrations, they were found to have no significant effect on the emulsion stability when 50% water-in-oil emulsions were used. These emulsions were stable for more than 4 weeks. The anionic HMWSPs, coded as A1, A2, and A3, in Refs.[64–66], were:

A1: Acrylic acid/lauryl methacrylate copolymer, (mol ratio 25:1, molecular weight = 4 kD);

A2: Acrylic acid/lauryl methacylate copolymer (mol ratio 8:1, molecular weight = 3 kD);

A3: Acrylic acid/stearyl methacrylate copolymer (mol ratio 8:1, molecular weight = 3 kD).

A cationic HMWSP, a copolymer of dimethyldiallylammonium chloride and butyl acrylate, (mol. ratio 25:1, molecular weight = 6 kD, see Refs.[61,62]) was observed to have no effect in concentration range tested.

CONCLUSIONS

Test tube emulsification tests showed that the period over which the crude oil was in contact with the aqueous phase was important for emulsion formation and emulsion stability. Addition of synthetic surfactants leads to the formation of highly stable emulsions, which when aged, lead to oil phase separation on the top without any aqueous phase separation. Emulsion stability increased with increasing added surfactant concentration.

The emulsions were found to display different levels of stability depending on the composition of the oil sample. The light fractions of the oil produced relatively unstable emulsions whilst the heavy fractions formed emulsions very easily and they were remarkably stable. The ratio of water to oil where emulsification ceased to occur was found to be ca. 75% formation water content.

It was shown that enhanced separation could be achieved through the application of high pressure. The addition of carbon dioxide from a 50-bar supply did not have any effect, adverse or otherwise, on this improvement.

Tests with application of a high-voltage electrostatic field on the emulsions revealed that lower-stability emulsions at least are susceptible to this method of separation. Further work will have to be performed with the more stable emulsions to assess the effectiveness of separating them. A number of surface-active copolymers were used as de-emulsifiers, but they did not show any tendency to enhance the separation. The addition of surfactants is not always desirable since they can cause additional problems in downstream processing. These results indicate that although high pressure accelerates oil-water separation, it is nevertheless still a very slow process compared with the de-emulsifier system recently disclosed by Akay, Pekdemir and Vickers.[67]

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