Droplet crystallization in water-in-crude oil emulsions: influence of salinity and droplet size

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ABSTRACT

Ice crystallization in confined spherical geometries is investigated experimentally at ambient pressure conditions. Water-in-crude (w/o) oil emulsions are formed by homogenization of an acidic North Sea crude oil with water or brine, at aqueous phase fractions ranging from 1-30 wt.% and varying electrolyte contents. Ice-in-oil dispersions are formed from the emulsions by cooling, and provide a justified analogue to gas hydrate formation in water-in-crude oil emulsions, due to analogous wettability conditions that govern agglomeration. Nuclear Magnetic Resonance (NMR) spectroscopy and digital video microscopy (DVM) imaging establish droplet size distributions (DSDs) and mean droplet diameters, and demonstrate emulsion stability with an absence of coalescence over extended time durations. Differential Scanning Calorimetry (DSC) establishes the crystallization temperature of the dispersed water droplets. It is demonstrated that the crystallization temperature decreases with a decreasing length scale of the dispersed water droplet phase, in accordance with theoretical knowledge.

Key words: crude oil, water-in-crude oil emulsions, differential scanning calorimetry, nuclear magnetic resonance, droplet size distribution, emulsion stability

1. INTRODUCTION

Conventional crude oil reserves are being rapidly depleted worldwide. As a result, industrial and academic scientists are working to develop unconventional petroleum reserves, especially petroleum reserves located on the Arctic shelf, also known as the continental shelf of Russia. Because of cold climatic conditions and concomitant slow biodegradation, the pristine Arctic shelf region is inherently vulnerable to a range of ecological risks, in particular marine toxification, fish spawning, avian habitat, vegetation health and mammalian welfare. Petroleum reservoir development on the Russian continental shelf requires new technologies for production and transportation of crude oil at low temperatures and under a heavy presence of ice float. Specifically, flow assurance becomes a vital consideration. Waxy crude oil contains elevated contents of saturates (including paraffin waxes), while heavy, and extra heavy crude oil contains, high concentrations of asphaltenes, and/or resins, causing extreme flow resistance at Arctic thermal conditions due to severely high viscosity or highly complex fluid rheology. At low temperatures, deposition of paraffin waxes on inner pipe wall surfaces serves to reduce effective cross sectional flow areas, resulting in increased pressure drops across axial pipeline distances, eventually causing complete flow blockage in the absence of implemented remediation measures. Successful management of paraffin deposition during transport requires dedicated capital and operational investment in pigging and pumping facilities[1]. Subsequent to water breakthrough, choke valve turbulence or high shearing exerted during flow lead to emulsion formation from the two separate phases: water and crude oil[2]. Water-in-crude oil emulsion formation is a serious issue in the petroleum transport industry; the emulsions are stabilized by indigenous surfactants. Water may originate from secondary or tertiary injection, or may be naturally produced from formation waters present in water drive reservoirs. In addition, water is present during washing out of contaminants in crude oils and during steam injection for fractionation improvement[1].

In the crude oil production industry, gas hydrates are of substantial importance. Gas hydrates are crystalline solids that assemble from water and gas molecules. In-situ formation of solid gas hydrate plugs poses a risk to subsea crude oil transportation, especially at in-situ production conditions in which multiphasic mixtures of water, gas and liquid oil are subjected to low temperature and elevated pressure conditions. Due to the crystalline nature and limited

solubility of hydrates, formation of hydrates may lead to blockage of long-distance transport pipes, such as in polar geographic regions or on the cold seabed[3]. Gas hydrate deposition occurs because of solidification, serving to reduce the effective pipeline diameter, which can restrict and eventually clog the flow. Another issue often ignored or unacknowledged is that gas hydrates are highly flammable and can decompose explosively[4]. However, even in the absence of a chemical detonation, gas hydrate dissolution by depressurization, accompanied by gas expansion, can potentially result in the formation of hazardous solid projectiles ahead of an expanding gas segment. It has therefore been traditionally desirable to completely avoid hydrate formation in petroleum production systems. Hence, thermodynamic inhibitors such as methanol are often added to subsea petroleum transport streams to prevent hydrate formation. However, a promising new alternative technology is to stabilize the formation of gas hydrates within the dispersed phase of water-in-oil emulsions, and exploit the presence of indigenous or synthetic surfactants at the water-oil interface to prevent agglomeration, deposition, and plugging of solid hydrates. If such a new subsea production technology can be successfully developed and quality assured, safe transport of colloidal gas hydrate particles to receiving facilities would be ensured. This new subsea technology necessarily encompasses controlled volumetric gas contraction and expansion, associated with hydrate formation and dissolution, respectively.

Emulsion and dispersion stability are essential criteria in preventing hydrate plugging in transport pipes[5]. The risk of hydrate agglomeration is reduced when emulsion stability increases. Moreover, natural surfactants such as asphaltenes and resins and other components like waxes and solid particles present in crude oil play a major role in emulsion stability and in hydrate agglomeration and plugging because interfacial tensions (or interfacial energies) are changed due to the presence of these components[6]. In the case of particle stabilization, the fraction of bare interface is reduced, and particles provide a mechanical barrier against agglomeration. Furthermore, the type and concentration of surfactant in crude oil affects hydrate formation[7,8]. Thus, the type of stabilizer affects hydrate formation. For effective hydrate management strategies in water-in-oil emulsions, the amount of water present in the emulsion plays a crucial role[9]. Finely dispersed water-in-oil emulsions assist in mitigating gas hydrate blockages[10]. Thus, droplet size of water-in-oil emulsion plays an essential role in hydrate management strategies[11]. The smaller the droplet dimension, the lower is the observed freezing temperature. The observed freezing temperature is substantially lower than the liquidus temperature. During cooling,

droplets dispersed in emulsions are expected to freeze and depending on their composition (i.e. concentration and type of salt), they will either completely solidify at the same temperature or not. Observed freezing temperatures are lower than the melting temperature, and they are found to be scattered about a mean temperature referred to as the most probable freezing temperature of the droplets[12]. The generation of ice nuclei requires cooling of the sample well below the bulk ice–liquid water equilibrium temperature, namely, 0 ºC for the case of de-ionized water. Therefore, as liquid water still exists in a metastable state below 0 ºC, it can be described as supercooled water. The homogeneous nucleation temperature of liquid water is generally accepted to be approximately -39 ºC for the case of de-ionized water. Below this temperature, even finely dispersed water droplets will freeze instantly. The presence of bulk water in the emulsion will give a signal at a temperature higher than the one obtained for dispersed water (around -20 ºC for bulk water). Another point that the shape of the signals is also different. This can be attributed to the manner in which the material solidifies either in bulk or in dispersed phases[19-24].

Emulsion characterization is an essential analytical focus area within the petroleum industry. The objective of the current report is to investigate the influence of droplet size, water content and salinity on crystallization of water droplets confined to water-in-crude oil emulsions. Ice-in-oil dispersions are studied as an analogue to hydrate-in-oil dispersions, due to difficulty in obtaining precision scientific measurements at elevated pressures. Utilization of ice to emulate the interfacial activity of gas hydrates is justified due to similar wettability conditions, which effectively govern interface activity.

2. MATERIALS AND METHODS

2.1. *Materials*

An acidic North Sea crude oil was first heated to 60 ºC and then manually shaken to ensure a uniform distribution of components. Subsequently, the oil was subsampled into 1 liter bottles and stored at room temperature. The oil was characterized with respect to ASTM D2007 SARA (Saturates, Aromatics, Resins and Asphaltenes)[13] analysis, emulsified water content,

density, total acid number (TAN)[14] and total base number (TBN)[15]. The analytical data is presented in Table 1.

MQ water (18.2 MΩ at 25 °C), analytical grade sodium chloride and calcium chloride were used for model brine with 3.5, 5, and 7 wt. % of salt.

Table 1. *Physical and chemical characteristics of the crude oil [16]*

Characterization parameter	Content
Saturates (wt %)	37.4 ± 0.5
Aromatics (wt %)	44.1 ± 0.5
Resins (wt %)	16.1 ± 0.6
Asphaltenes (wt%) (hexane-insoluble)	2.54 ± 0.03
Emulsified water (wt %)	0.06 ± 0.01
Density (g/cm^3, 20 °C)	0.934 ± 0.001
Total acid number, TAN (mg KOH/g)	2.15 ± 0.02
Total base number, TBN (mg/g)	2.81 ± 0.04
Dynamic viscosity (mPa·s, 20 °C)*	317.5 ± 0.1

* Determinated by rotation viscosimetry technique at shear rate $\dot{\gamma} = 100 \ s^{-1}$.

2.2. Methods

2.2.1. Emulsion Preparation

Water-in-oil emulsions (30 mL total volume) are prepared in glass vials by using a T25 digital IKA disperser with four-blade propeller at 2000 rpm and emulsification time of 5 and 15 min. An Ultra-Turrax T 25 Digital IKA with a S25N18G shaft is used at 8000 rpm for 5 min in order to create small droplets. The emulsion concentration (water cut or fraction) used was 1, 5, 10, 20 and 30 wt. %.

2.2.2. Nuclear Magnetic Resonance (NMR)

A low-field nuclear magnetic resonance spectrometer (MARAN Ultra spectrometer 23 MHz, Oxfords instruments, UK) is used for determination of droplet size distribution (DSD), average droplet size and water content in the emulsions immediately after preparation without requiring dilution or spreading. The measurements are performed at 25 °C on a 3.65 mL

emulsion sample placed in a 18 mm diameter glass tube. The measurements are based on methodology previously developed by Opedal et.al.[17]. The NMR technique is utilized to analyze emulsion samples with water contents greater than 10 wt. %, due to the required signal sensitivity of the NMR method.

2.2.3. *Digital video microscopy (DVM)*

A digital video microscope Eclipse ME600 (Nikon, Japan) mounted with a CoolSNAP-Pro camera is used to obtain visual images of the prepared emulsion samples immediately after emulsification and after 3 thermal cycles in the DSC at 50X amplification. Cover glass was not placed on the samples in order to avoid perturbation of the formed emulsions. The digital images are analyzed by Image-Pro Plus 5.0 (Media Cybernetics) software in order to obtain DSDs.

2.2.4. *Differential scanning calorimetry (DSC)*

A differential scanning calorimeter DSC Q2000 (TA Instruments, USA) is used to study water-in-oil emulsions and brine samples. Application of DSC allows acquisition of thermograms in which the acquired crystallization signal corresponds to a Gaussian-shaped peak. Cooling of the system from 20 °C to -90 °C is achieved using nitrogen as a purge gas at a continuous flow rate of 50 mL/min. An empty sample pan is used as a reference in order to sequester the measurement signal originating from the sample. The sample weight is adjusted between 10 and 20 mg. Three thermal cycles are performed to obtain crystallization thermograms, which provide experimental evaluation of the emulsion freeze/thaw stability at standard atmosphere pressure. Crystallization points are determined from peak maximum temperatures on the thermograms determined using the TA Universal Analysis 2000 software.

3. RESULTS AND DISCUSSION

3.1. Cooling rate

After sample pans are loaded into the DSC cell and thermal equilibration is attained, the examined system exists in a state of thermal equilibrium prior to start of measurements. Any conditional changes (temperature, for example) lead to the system being removed from a state of equilibrium. With time, the sample will attain equilibrium again at the new ambient conditions (a new temperature, for example). The time required for reversion to equilibrium is called the system relaxation time, with a corresponding system relaxation rate. The system relaxation rate

must be greater than the rate of temperature change for equilibrate processing of the sample. In other words, the lower the scanning rate, the higher is the probability of maintaining an equilibrium process within sample. However, reduced scanning rates lead to a reduction in signal-noise ratio and associated data quality. Therefore, reduced scanning rates exert a negative influence on measurement accuracy. Conversely, high scanning rates give rise to significant temperature gradients within the emulsion sample volume[18].
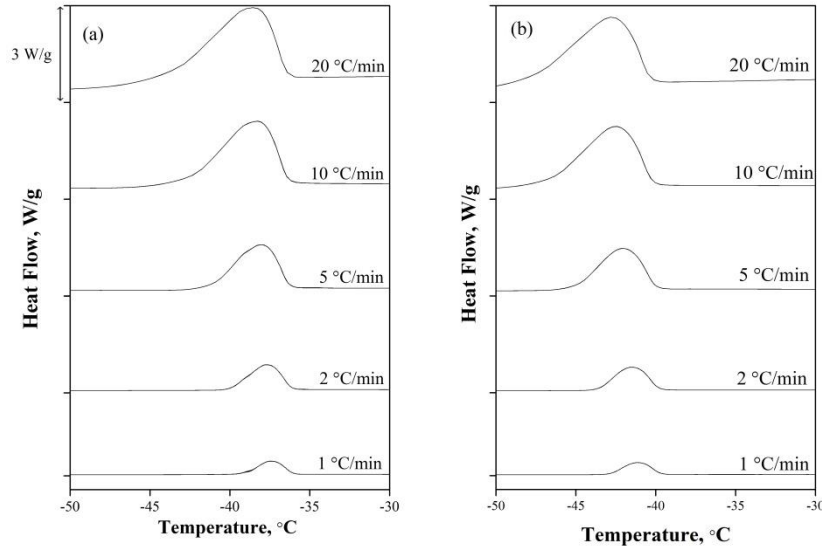
Fig. 1 Thermograms of w/o emulsions ($\varphi = 0.2$) cooled from 20 to -90 °C at various cooling rates and different water phase: (a) – MQ water, (b) – 3.5 wt. % NaCl solution

In this investigation, various scanning rates (1, 2, 5, 10, and 20 °C/min) are used for the emulsion samples in order to broadly characterize the influence of thermal history on freezing temperatures and heat of crystallization, which is proportional to peak areas on experimental thermogram curves (Fig. 1).

Crystallization thermograms exhibit peak tailing phenomenon and a small negative shift in the location of the crystallization signal by several tenths of a degree with an increase in cooling rate. The shift is distinctly evident and even more pronounced at elevated scanning rates (10 and 20 °C/min). Estimates of heats of crystallization and values of crystallization temperatures at various scanning rates are given in table 2.

Table 2. *Change of signal depending on scanning rate*

Scanning rate	Heat of crystallization (J/g)		Crystallization temperature (ºC)	
	MQ water	3,5 % NaCl	MQ water	3,5 % NaCl
1	282	267	-37.5	-41.2
2	287	266	-37.7	-41.5
5	284	265	-38.0	-42.0
10	280	266	-38.2	-42.4
20	284	262	-38.6	-42.8

Estimate of crystallization heat suggests that scanning rate also does not influence on that parameter. Experimental value of heat of crystallization is less than the standard value for water (330 J/g). The difference lies in the integrated difference of solid and liquid heat capacities from the onset temperature (~-40 °C) to standard conditions (25°C).

The increase of latent heat sensitivity with increased cooling rate is caused by a much larger heat flow signal associated with a very small corresponding increase in signal noise. It's therefore important to choose an optimum cooling rate to maintain a good sensitivity and resolution at the same time. The resolution is improved due to sensitivity for a lower cooling rate, which is expressed by the peak maximum. In other case, the strong decrease of cooling rate may lead to enlargement of the experiment time.

Therefore, an preferable for our investigations cooling rate is 5 °C/min, according to Dalmazzone's recommendations[19, 20]. That value of the scanning rate is providing a good sensitivity, resolution and short time of experimental run.

3.2. Stability of crude oil emulsions

The most critical property of emulsions is phase stability against sedimentation and coalescence processes. Therefore, water-in-crude oil emulsions are investigated using optical microscopy and differential scanning calorimetry.

Fig. 2 illustrates photomicrography of water-in-crude oil emulsion prepared at 2000 rpm for 5 min with 20 wt. % brine (3.5 wt. % NaCl in water), which is obtained immediately after preparation and after 2, 4, 8, 48, 96 hours.
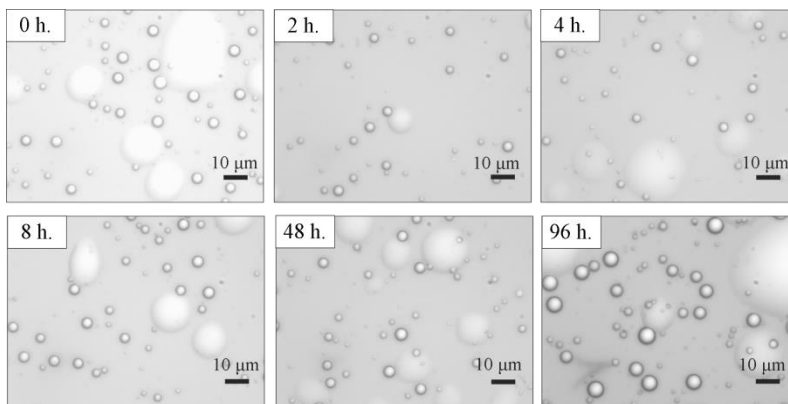

Fig. 2 Microphotograms obtained for 96h. for emulsion prepared with 3.5 wt.% solution of NaCl at 2000 rpm for 5 min; water phase contain: 20 wt.%. Amplification is in 50 times.

The droplet size remains constant during the entire testing period of 96 hours, with a mean droplet diameter of approximately 3-4 μm. These results indicate emulsion stability for 96 hours of study. In order to experimentally corroborate the findings, the emulsion systems were also investigated by DSC for 96 hours. Crystallization thermograms are shown on Fig. 3.
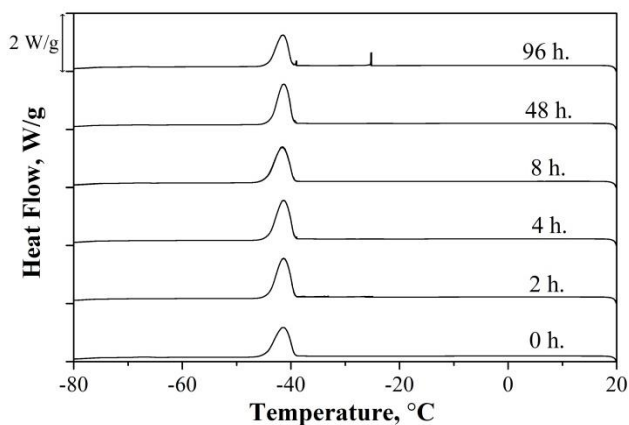
Fig. 3 DSC crystallization thermograms obtained at cooling rate 5 °C/ min for emulsion prepared with 3.5 wt. % NaCl solution at 2000 rpm for 5 min; water phase contain: 20 wt. %.

DSC curves demonstrate high emulsion stability during the 96 hour test period as all crystallization peaks center around -41 °C and exhibit highly similar heats of crystallization, which are equal in value to the peaks areas. Differences between heats of crystallization are not greater than 6%. The DSC trends in totality are in agreement with the images obtained by DVM. The absence of a shift to higher or lower temperature is associated with constancy in droplet diameter, confirming an absence of droplet coalescence during the test period. However, a narrow solidification peak is evident at -25 °C, which likely correlates with crystallization of bulk free water at the bottom of the pan. It is important to indicate that the signal in Fig.3 located between -40 and -46 °C is associated with the normal highest crystallization temperature of pure water [20, 21, 22]. As shown in series of base contributions[19, 20, 24, 25], the presence of bulk phase in the emulsion will give a signal at a temperature higher than the one obtained for dispersed material. Freezing point of bulk water is around -20 ºC and -35÷-45 ºC for dispersed water. In the sample of pure crude oil no water was detected by DSC measurements.

The 2nd corroborative evidence of emulsion stability is that the 3 consecutive cycles of DSC measurements do not exert any influence on the crude oil emulsions, as all 3 curves have a well reproducible and super-imposable Gaussian-like shape. These observations confirm that water droplets do not undergo changes in diameter during repetitive cooling/heating processes.

3.3.Droplet size

Several factors, including chemical composition, phase composition, temperature, interfacial tension and energy input during preparation exert an influence on the properties of obtained w/o emulsions. The most significant properties of water-in-oil emulsions are droplet size distribution (DSD) and mean droplet size of the emulsion.

The influence of emulsification time on droplet size is investigated on water-in-crude oil emulsions prepared at 2000 rpm for 5 and 15 minutes with a 3.5 % solution of NaCl as the aqueous phase. DSDs and mean droplet sizes are determinated by optical microscopy and NMR measurements. Tenuous differences between measurement results are often due to the fact that NMR is a volume based measurement. DVM does not consider the density of the emulsions layers.
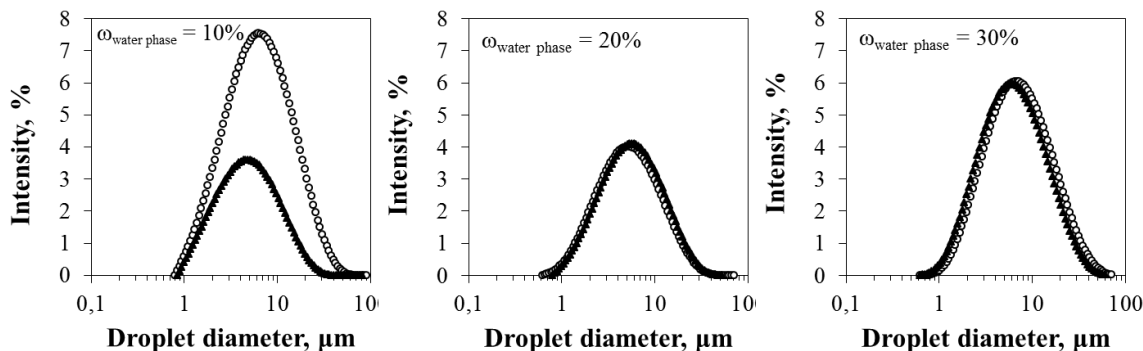
Fig. 4 Droplet size distribution for water-in-crude oil emulsion measured by NMR (water phase: 3.5 wt. % solution of NaCl) prepared for 5 min (circles) and 15 min (triangles) at 2000 rpm.

Fig. 4 shows droplet size distributions measured by Nuclear Magnetic Resonance. NMR experiments are performed immediately after emulsion preparation. A mean droplet size distribution centered around 3-4 μm is observed for all emulsions prepared with 3.5 wt. % NaCl solution at 5 and 15 minutes, which is in quantitative agreement with images obtained by optical microscopy (Fig.5). Images of water-in-crude oil emulsions prepared at various emulsification times are obtained at 50X amplification.

Experimental results indicate that increased emulsification time from 5 to 15 min does not have a profound effect on water droplet size in emulsions. The crystallization temperature of water droplets depends strongly on droplet size. Larger water droplets exhibit higher crystallization temperatures, according to Clausse et al. [24, 25], who ascertained theoretical and empirical correlations confirming that droplet size increases exponentially with peak crystallization temperature, based on an assumption of homogeneous nucleation and instantaneous freezing of a droplet upon nucleus formation.
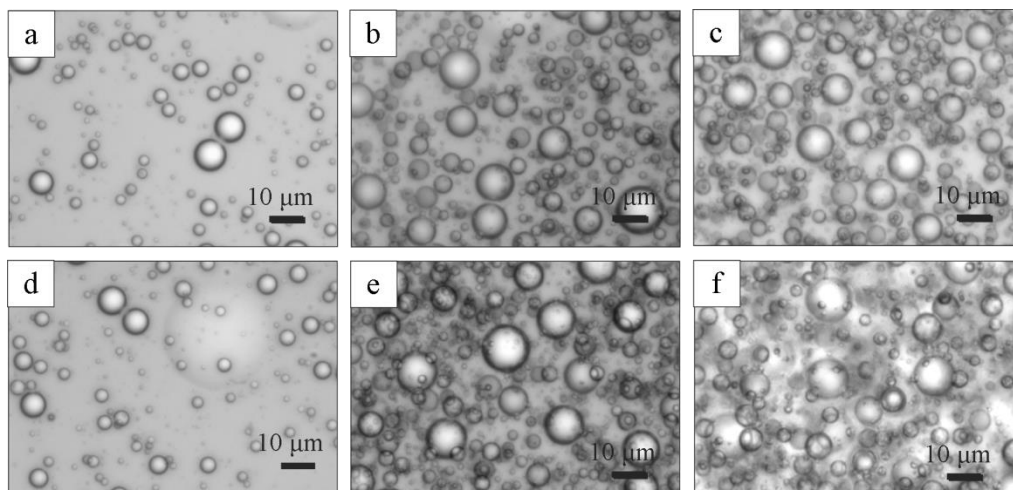
Fig. 5 Microphotograms for emulsion prepared with 3.5 wt. % solution of NaCl at 2000 rpm for 5 min(a-c) and for 15 min (d-f); water phase content: a, d – 10 %; b, e – 20 %; c, f – 30 %. Amplification is 50X.

Because a calorimetric signal is obtained from the crystallization of each droplet, and because the solidification temperature is related to droplet size, crystallization thermograms effectively represent DSDs, although the stochastic nature of homogenous nucleation also contributes to some extent to DSC peak broadening. For instance, even in the case of a perfectly monodisperse droplet size distribution (DSD), the stochastic nature of homogenous nucleation will ensure a finite thermogram peak width, even after correcting for instrumental heat signal lags. In practice, crystallization temperature is determined as maximum intensity on an experimental DSC thermogram. This temperature corresponds to the maximum occurrence frequency in the droplet size distribution.

Thermograms obtained during three DSC cycles of an emulsion sample are reported in Fig. 6. The emulsions are prepared by homogenization for 5 or 15 min and contain 3.5 wt. % of NaCl in water. The emulsions are the water phase characterized by a water crystallization peak centered around -41 to -42 °C due to similar mean droplets diameters of all emulsions. It is confirmed that emulsification time does not have significant impact on droplet size. This signal location is typical for the crystallization of small sized (micron-scale) water droplets [23,12].

The most effective technique for altering the size of water droplets is to vary the emulsification rate, quantified by the rotational rate of the homogenizer. When greater energy is applied to the system, smaller droplet diameters are formed and the specific interfacial area is

increased. In this investigation, emulsions are prepared with 3.5 wt. % NaCl solution as a water phase, and are homogenized at 2000, 8000, 16000 and 24000 rpm for a duration of 5 minutes. The mean droplet diameter is calculated from the droplet size distribution for emulsions with water content from 10 to 30 % obtained by NMR and optical microscopy for emulsion samples obtained at 2000 and 8000 rpm (Fig.7). The water droplets of emulsions prepared at 16000 and 24000 rpm are very small and it is not possible to prepare images of the samples using optical microscope (Table 3).
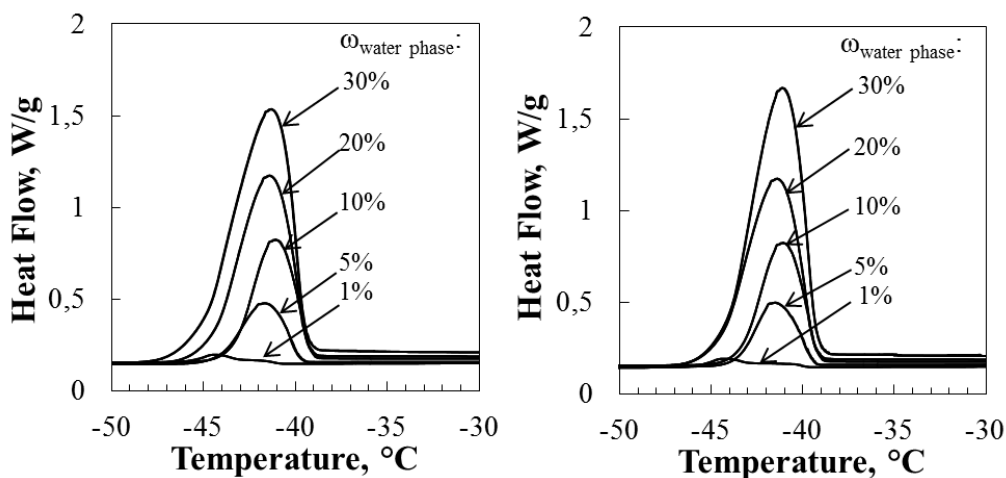
Fig. 6 Thermograms of crystallization for the crude oil emulsions prepared with 3.5 % solution of NaCl at 2000 rpm for: (a) – 5 min, (b) – 15 min.
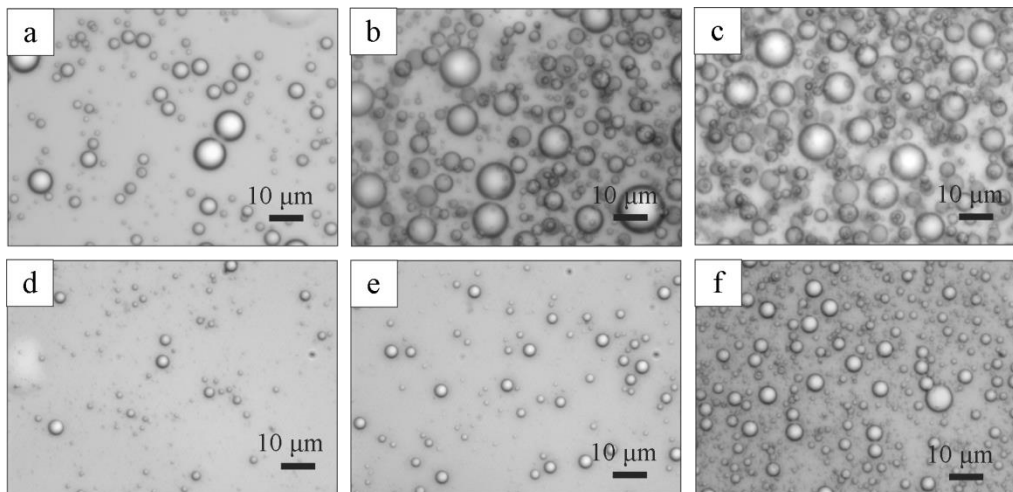

Fig. 7 Emulsion microphotograms prepared with 3.5 wt. % solution of NaCl for 5 min at 2000 rpm (a-c) and 8000 rpm (d-f); contain of water phase: a, d – 10 %; b, e – 20 %; c, f – 30 %. Amplification 50X.

Table 3. Values of mean droplet diameters of emulsions obtained with 3.5 % solution of NaCl at various emulsification rates, obtained by DVM and NMR.

Content of water phase, %	$\bar{d}$ (µm) by DVM		$\bar{d}$ (µm) by NMR			
	2000 rpm	8000 rpm	2000 rpm	8000 rpm	16000 rpm	24000 rpm
1	8.0	2.7	−	−	−	−
5	3.7	2.4	−	−	−	−
10	4.8	6.1	8 ± 1	4.7 ± 0.2	5.1 ± 0.5	6 ± 1
20	4.5	3.2	8.1 ± 0.2	3.6 ± 0.5	4.0 ± 0.1	4.0 ± 0.3
30	4.6	5.1	9.6 ± 0.3	6.1 ± 0.6	3.4 ± 0.3	4.0 ± 0.2

NMR and DVM data illustrate that increasing the emulsification rate from 2000 to 8000 leads to a reduction in droplet size by a factor of two. Based on data obtained by nuclear magnetic resonance, it is surmised that a further increase in homogenization rate from 16000 rpm to 24000 rpm does not have a significant effect. As further proof of the observed results, emulsion samples are analyzed by DSC. Fig. 8 presents thermograms of emulsions obtained with 3.5 wt. % NaCl in the aqueous phase at various emulsification rates. Certain differences are observed between signals of crystallization. The signals represent an overlay of several individual Gaussian-like peaks, obtained for each emulsified water content corresponding to each droplet size. The solidification temperature decreases by ~1 °C for each increase in emulsification rate, within this range. Observed differences in freezing transition temperature originate from differences in droplet size distributions. Mean droplet size becomes smaller when more energy is applied (higher speed of emulsification) to the system. The existence of a single narrow characteristic crystallization define apex in conjunction with a highly symmetrical peak shape in all thermograms demonstrates conclusively the largely monodisperse character of the prepared emulsions. Moderate variation in total peaks areas may indirectly stem from differences in sample mass prepared for the DSC.
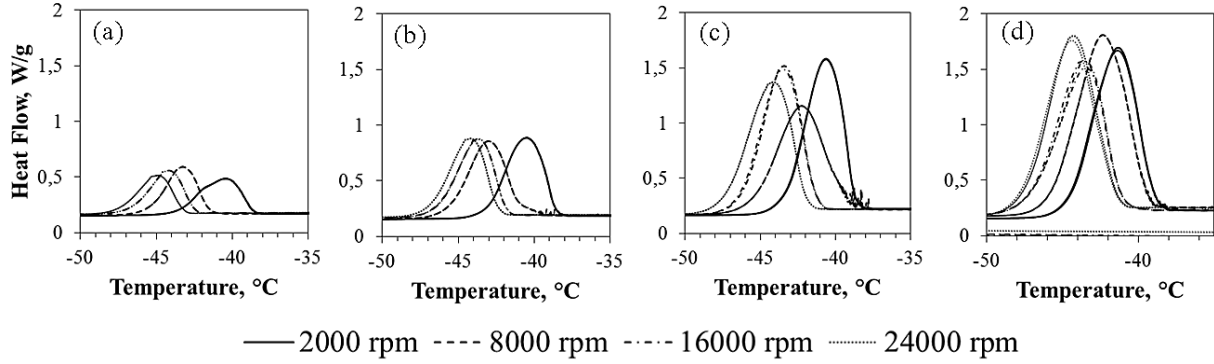
Fig. 8 Crystallization thermograms for crude oil emulsions obtained with 3.5% solution of NaCl at different emulsification rate for 5 min. Content of water phase: (a) – 5%, (b) – 10%, (c) – 20%, (d) – 30%.

Various crystallization temperatures corresponding to the average droplets diameters ($\bar{d}$) in the emulsions were obtained. Figure 9 shows the results for emulsions obtained with 3.5 wt. % NaCl in the aqueous phase. It is apparent that decrease of mean droplet diameter leads to the depression of crystallization temperature. This behavior correlates with the nucleation theory positing that the smaller the droplets sizes (i.e. the smaller their volume), the lower the crystallization temperature is. This theoretical approach is based on the fact that to induce freezing, the formation of an ice nuclei is required. Due to capillary phenomena, it is possible to demonstrate that the relation between the water droplet radius r and the freezing temperature T_{cr} is given by the following equation:

$$r^3 = \frac{3\dot{T}}{4\pi} \cdot \frac{0.69}{\int_{T_m}^{T_{cr}} J dT}$$

with the nucleation rate J given by:

$$J = A \cdot exp\left[\frac{16\pi\gamma^3 V_i^2}{3L_m^2 ln^2\left(\frac{T}{T_m}\right)} \frac{1}{kT}\right]$$

where $\dot{T}$ is the scanning rate (K·s⁻¹); A – is the pre exponential factor in the expression of the nucleation rate, (s⁻¹·m⁻³); K is the Boltzmann constant (N·m·K⁻¹); γ is the interfacial tension between water and the ice nuclei (N·m⁻¹); V_i – is the molar volume of the germ (m³·mole⁻¹); L_m – is the molar melting heat (N·m·mole⁻¹); and T_m is a melting temperature[25].

15

It is preferable to determine an empirical correlation between r and T_{cr} by comparing the most probable crystallization temperatures obtained from DSC analysis and the mean droplet size obtained by another analytical technique[25].
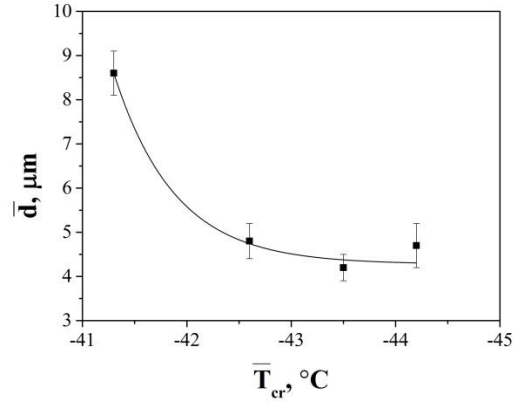

Fig. 9 Correlation curve obtained between the mean droplet diameter $\bar{d}$

and their most likely temperature of solidification T_{cr} for emulsions prepared with 3.5 % solution

of NaCl

3.4. Composition of water phase

Droplets dispersed in emulsions are expected to undergo a freezing process that depends on the overall phase composition and the thermal history of the process. If the degree of polydispersity is low, a Gaussian shape is anticipated on the thermogram peak. On the other hand, if an emulsion is constituted by a wide range of droplet sizes, it is anticipated that more than one signal may be observed on the thermogram, and the shape of the peak signals may be asymmetrical[24].

Mineralization and composition of the aqueous phase exert a stark influence on the stability of water-in-crude oil emulsions. As a rule of thumb, the stability of this system rises with an increase in mineralization[25]. The effect of water phase salinity on oil transportation is an important factor in preventing gas hydrate formation. Salt is a thermodynamic inhibitor of gas hydrate formation, due to its colligative solution properties. The presence of dissolved salt in water leads to an increase in the ionic strength of the aqueous phase, and causes a colligative effect that lowers the equilibrium temperature of ice or hydrate formation. This is the same phenomenon as freezing point depression of water by addition of salt[26].

Fig. 10 demonstrates a weak dependence of water droplet size on salt concentration. Mean diameter becomes slightly smaller with increasing salt concentration. However, these values vary from 5 to 2 μm. Droplets with higher sizes are indicative for emulsions prepared with deionized water as a water phase. Emulsions containing salt solutions are characterized by very similar droplet diameters.
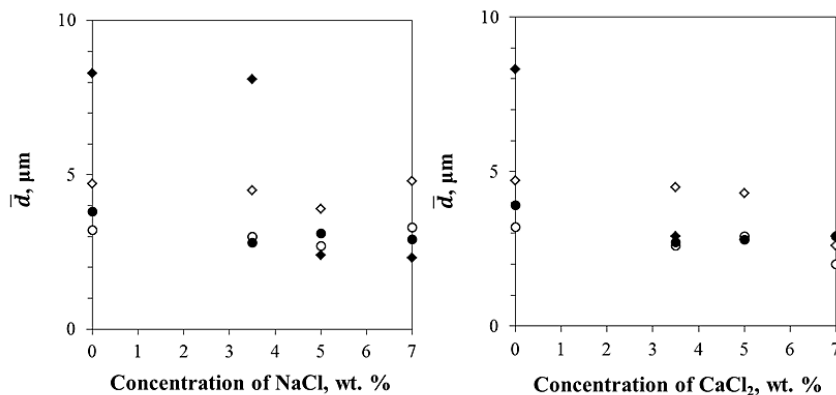

Fig. 10 Depending between mean droplet diameter, obtained by DVM (white points) and NMR (black points), and salt concentration in water phase for emulsions obtained at 2000 rpm (rhombohedral) and 8000 rpm (circles)

Crystallization thermograms obtained by DSC for w/o emulsions with different types of water phase prepared at 2000 rpm for 5 min are show on Fig. 11. Solidification peaks of pure deionized water are located at a temperature close to -38 °C. For emulsions containing aqueous solutions of sodium and calcium chlorides, solidification peaks attributed to droplet crystallization are observed in the vicinity of -41 °C. Observed shifting of the apex of the crystallization thermograms may indicate that emulsions prepared with de-ionized water have a larger distribution of droplets than emulsions in which droplets form in the presence of salts. These results correlate with data obtained by NMR and DVM.

Similar experiments are conducted for emulsions prepared at 8000 rpm for 5 minutes. Results are shown in Table 4. In this case, the crystallization signal is observed to shift by several degrees for all emulsions due to a smaller droplet size distribution originating from use of a higher homogenization rate. The crystallization temperature of droplets is slightly lower in presence of sodium chloride than with calcium chloride in both cases due to the differences

between molecular weights of salts. Change from mass concentrations to molar concentration may demonstrate that concentration of NaCl in two times higher than CaCl at the same weight concentrations. That leads to shift of crystallization peaks on several degrees. It's related with the universal Raoult law. Theoretical value of ΔT for 3.5 % NaCl solution is -2.3 ºC, for CaCl$_2$ with the same concentration is -1.2º C.
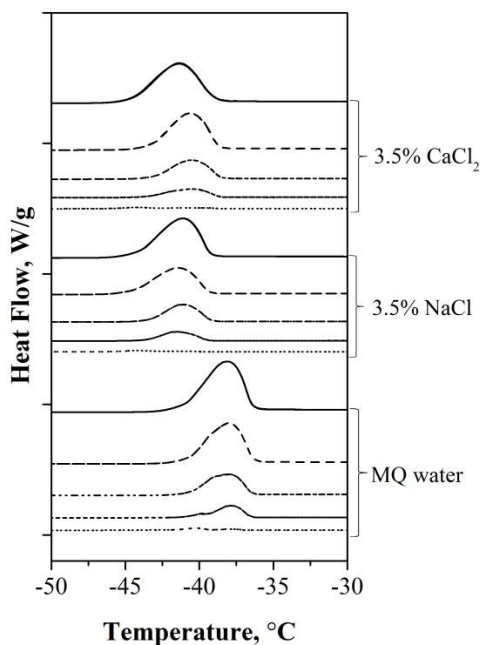

Fig. 11 Crystallization thermograms for water-in-crude oil emulsions prepared with different types of water phase at 2000 rpm where: (—) – 30 % wc, (− −) – 20 % wc, (−···) – 10 % wc, (- - -) – 5 % wc, (···) – 1 % wc

Table 4. Crystallization temperatures of droplets in emulsions obtained at 8000 rpm for 5 min with different types of water phase

Water phase	Crystallization temperature of droplets, °C				
	1 % wc	5 % wc	10 % wc	20 % wc	30 % wc
MQ water	-39.6	-39.1	-39.0	-38.7	-38.6
3,5 % NaCl	-46.4	-43.3	-43.0	-42.3	-42.4
3,5 % CaCl$_2$	-43.6	-42.4	-41.8	-41.7	-41.4

Aqueous phase salt concentration exerts a strong influence on droplet crystallization. Fig. 12 presents the observed dependence of average crystallization temperature on electrolyte concentration. Droplet freezing transition temperature decreases by 2-3 °C for every increase in salt concentration of 1.5 – 2 wt. %. This is the case for w/o emulsions obtained at 2000 and 8000 rpm, which is also consistent with increased emulsification rates serving to reduce the freezing temperature due to differences in droplet size distribution. The concentration of salt within the water droplet increases with ice formation, due to a sequestration of salt away from the growing ice crystals, and this up-concentrating of salt in the mother liquor drastically impacts the growth rate. In fact, as the temporal salt concentration increases locally due to the up-concentrating effect, the local equilibrium temperature is further shifted to lower values, leading to less sub-cooling, and slowing the ice formation process[26].
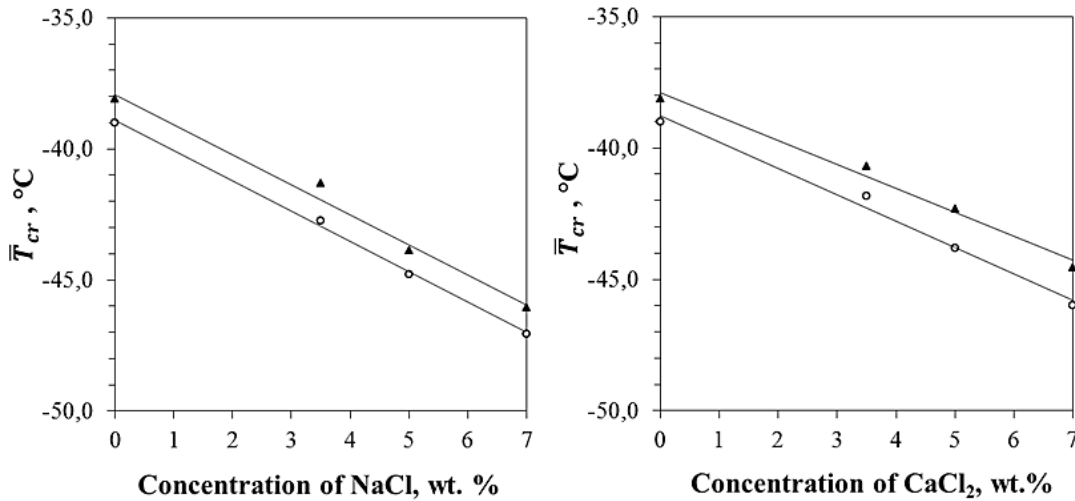

Fig. 12 Correlations between average crystallization temperatures of droplets and salt concentration in water phase for water-in-crude oil emulsions obtain for 5 min at 2000 rpm (triangles) and 8000 rpm (circles)

CONCLUSIONS

Emulsion stability is an important criterion in preventing gas hydrate plug formation in subsea transport pipelines. The risk of hydrate formation is reduced when the emulsion stability increases. Mineralization and composition of the water phase, content of water and droplet size distribution all strongly influence the stability of crude oil emulsions.

In this work, correlation between droplet size distribution obtained by different methods, such as DVM and NMR, and crystallization temperatures of droplets in water-in-crude oil emulsions was established by DSC measurements. Furthermore, influence of water phase composition, i.e type of salt and salt concentration, on crystallization temperature of droplets was studied. Smaller droplets exhibit a lower crystallization temperature. Beyond a necessary emulsification time needed to form small droplets, additional emulsification time does not have any influence on emulsion stability nor crystallization temperature. Increasing the salt concentration drives a shift of the crystallization peak to lower temperature values by ~2-3 °C. Crude oil emulsions remain stable for 96 hours, indicated by an absence of droplet coalescence. Crude oil emulsions with water contents ranging from 1 to 30 wt. % remain stable after three cycles of DSC measurements and all curves have a well reproducible Gaussian-like shape. Finally, it is confirmed that emulsified water droplets do not change size during the cooling/heating process.

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REFERENCES

1. Keleşoğlu, S.; Pettersen, B.H.; Sjöblom, J. Flow properties of water-in-North Sea heavy crude oil emulsions. *Journal of Petroleum Science and Engineering* **2012,** *100*, 14-23.
2. Fingas, M.; et al. *The physics and chemistry of emulsions*. Environment Canada and Consultchem, Ottawa, Canada and US Minerals Management Service: *Herndon, Virginia,* **1993**.
3. Dahlmann, U.; Feustel, M. Corrosion and gas hydrate inhibitors having improved water solubility and increased biodegradability. U.S. Patent No. 7,435,845, 14 Oct. 2008.

4. Speight, J. *Handbook of Offshore Oil and Gas Operations*, *1st Edition*. Gulf Professional Publishing: Amsterdam, **2014**.

5. Lachance, J.W.; Sloan, E.D.; Koh, C.A. Effect of hydrate formation/dissociation on emulsion stability using DSC and visual techniques. *Chemical Engineering Science* **2008,** *63,* 3942-3947.

6. Sjöblom, J.; et al. Investigation of the hydrate plugging and non-plugging properties of oils. *Journal of Dispersion Science and Technology* **2010,** *31*, 1100-1119.

7. Fadnes, F.H. Natural hydrate inhibiting components in crude oils. *Fluid Phase Equilibria* **1996,** *117*, 186-192.

8. Kalogerakis, N.; et al. Effect of surfactants on hydrate formation kinetics. *SPE international symposium on oilfield chemistry*. Society of Petroleum Engineers, 1993.

9. Karaaslan, U.; Parlaktuna, M. Surfactants as hydrate promoters? *Energy & Fuels* **2000,** *14,* 1103-1107.

10. Creek, J.L. Efficient hydrate plug prevention. *Energy & Fuels* **2012,** *26*, 4112-4116.

11. Sloan, E.D.; Koh, C.A.; Sum, A. *Natural Gas Hydrates in Flow Assurance*. Gulf Professional Publishing: Amsterdam, 2010.

12. Raman, A.K.Y.; et al. Emulsion stability of surfactant and solid stabilized water-in-oil emulsions after hydrate formation and dissociation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2016,** 506, 607-621.

13. Hannisdal, A.; Hemmingsen, P.V.; Sjöblom, *J. Ind. Eng. Chem. Res.* **2005**, 44 (5), 1349–1357.

14. ASTM D664-95 (2001), Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration, *ASTM International*, West Conshohocken, PA, **2001**.

15. Dubey, S. T.; Doe, P. H. *SPE Reservoir Eng.* **1993**, 8 (3), 195–200.

16. Rodionova, G.; et al. Preparation and characterization of reference fluid mimicking behavior of North Sea heavy crude oil. *Fuel* **2014**, 135, 308-314.

17. Van der Tuuk Opedal, N.; et al. Methods for droplet size distribution determination of water-in-oil emulsions using low-field NMR. *Diffusion fundamentals* **2009,** *7*, 1-29.

18. Zhao, J.-C. Methods for Phase Diagram Determination. *Elsevier*, 2007.

19. Clausse, D.; et al. Morphology characterization of emulsions by differential scanning calorimetry. *Advances in Colloid and Interface Science* **2005**, 117, 59-74.

20. Dalmazzone, C.S.H.; Clausse, D. Microcalorimetry. In: Sjöblom J, editor. Encyclopedic handbook of emulsion technology. Marcel Dekker Inc: New York, **2001**, 327–348.

21. Mossop, S.C. The freezing of supercooled water. *Proceedings of the Physical Society. Section B* **1955,** *68*, 193.

22. Langham E.J.; Mason B.J. The heterogeneous and homogeneous nucleation of supercooled water. *Proc R Soc Lond A.* **1958**, *247*, 493.

23. Bogdan, A. Phase transitions in finely divided aqueous systems. *In: Hubbard AT, editor. Encyclopedia of surface and colloid science.* Marcel Dekker: New York, 2002, pp. 4002–305.

24. Clausse, D.; et al. A method for the characterization of emulsions, thermogranulometry: application to water-in-crude oil emulsion. *Journal of colloid and interface science* **2005,** *287*, 694-703.

25. Clausse, D.; Dalmazzone C. Freezing Within Emulsions: *Theoretical Aspects and Engineering Applications. Oil & Gas Science and Technology – Rev. IFP Energies nouvelles* **2014**, 69, No. 3, 415-434.

26. Delgado-Linares, J.G.; et al. Model water-in-oil emulsions for gas hydrate studies in oil continuous systems. *Energy & Fuels* **2013,** *27,* 4564-4573.