

Differential scanning calorimetry characterization of water-in-oil emulsions from Mexican crude oils

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Received: 26 January 2010 / Accepted: 25 May 2010 / Published online: 10 June 2010
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Abstract A simplified equation relating water droplet size distribution to crystallization temperature, determined from differential scanning calorimetry (DSC) curves of aqueous emulsions of petroleum is reported in this article. A series of water-in-oil (W/O) emulsions was prepared by dispersion of water in different Mexican crude oils; in a classical DSC experiment, these emulsions were submitted to a regular heating and cooling cycle within temperatures including freezing and heating of dispersed water. The Z-average diameters of the water drops (D_{dz}) were estimated this way and correlated with petroleum composition.

Keywords DSC · Water–oil emulsions · Mexican crude oils

Introduction

At the beginning of the twenty-first century, the world's high consumption of energy has provoked a rapid decline of light crude oil reserves. The production of heavy and super-heavy crude oils is ever increasing, and the problem of oil-in-water (O/W) emulsions, with a high concentration

of water and salts turning out to be an important issue. It is necessary to measure the different sizes of water drops dispersed in crude oil, and to design and evaluate chemical products for the desalting and dehydration of heavy and super-heavy petroleum; common techniques such as light scattering are not useful, however, because of the extra high opacity of crude oil continuous phase.

On the other hand, thermal analysis techniques are more frequently employed to characterize petroleum and its derivatives [1–3]. The thermal behavior and degradation of a wide variety of whole crude oils and their fractions, obtained by means of chromatographic or distillation methods, have been studied by thermogravimetric analysis [4, 5]. Similarly, differential scanning calorimetry (DSC) has shown to be a reliable method to elucidate some of the main features of the saturate, aromatic resins and asphaltenes constituting petroleum [6]. Only the characterization of dry samples of crude oil and derivatives are here reported; even if the event thermal methods had not been originally conceived for characterizing dispersed systems, some pioneer researches were performed, with the aim of investigating the solidification of drops dispersed in a continuous phase, by differential thermal analysis (DTA) and DSC. This last technique has turned out to be a very suitable method for studying the behavior of emulsions submitted to a temperature gradient [7]. The heats released or absorbed when solidification or melting takes place within an emulsion can be both detected and quantified by DSC. Nevertheless, if getting emulsion characteristics from DSC measurements were not obvious, this thermal technique constitutes one of the most suitable methods to investigate the stability and characteristics of water in petroleum emulsions. With the aim of solving this problem, Clause and Dalmazzone have proposed the use of the thermogravimetry, meaning the application of DSC, to

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determine the drop distribution of the aqueous phase and associated phenomena [8–15]. They have analyzed both the drop ice nucleation, and its kinetic behavior. These researchers have found that the experimental determination of the theoretic parameters is not allowable and, based on this, they have established an experimental correlation between the most likely solidification temperature of a droplet T^* , and the water drop size distribution obtained by microscopic analysis [8]. It is important to state that T^* is the main freezing temperature, as determined by Bigg [16], where 50% of the droplets of a specific droplet diameter are frozen [17]. This temperature parameter is also obtained by DSC.

With the aim of characterizing a series of emulsions of water dispersed in Mexican crude oils, a simplified equation was inferred in this study, relating the water droplet size distribution to the crystallization temperatures found by using the DSC curve. The statistical average D_{dz} was also calculated. It was, therefore, possible both, to compare the drop diameter distribution of water dispersed in different crude oils and to explain in which type of petroleum the stability of the water-in-oil (W/O) emulsion was higher.

Experimental methods

Materials

Mexican crude oils: samples of light (36° API), heavy (22° API) and super-heavy (17° API) petroleum belong to Mexican Gulf oil field.

Physical testing

Samples of Mexican crude oils were first submitted to a series of characterizations to determine their main physical features. Kinematic viscosity was measured following the ASTM-D 445 method. Salt and water contents in crude oil were determined, respectively, according to the ASTM-D 3230-06 and ASTM-D 4006-07 procedures. In the case of pour points, they were evaluated according to the ASTM-D 97 method. Wax content was evaluated in accordance with the UOP-46 norm. SARA composition was obtained by precipitation of asphaltene with n-heptane, and maltenes were separated through the HPLC method with Water Spherisorb NH₂ Column 10 μm (20 × 250 mm) Preparative [18]. Main characteristics and properties of crude oils are reported in Table 1.

DSC sample preparation

It has been shown that thermal methods, such as thermogravimetry (TG) and differential scanning calorimetry

Table 1 Main physical feature of mexican crude oils

Type of crude oil	Light	Heavy	Super-heavy
API density	36.00	21.75	16.78
Salt (lb/1000 bls of crude oil)	2.66	7.66	21.0
Water by distillation/vol.%	<0.10	0.10	0.30
Kinematic viscosity/mm ² s ⁻¹	5.27	201.5	2319.15
Pour point/°C	−45.0	−36.0	−20.0
Wax content/wt%	3.10	4.02	4.32
SARA analysis/wt%			
Saturates	11.88	8.14	9.30
Aromatics	6.21	8.79	13.53
Resins	81.01	73.42	61.74
Asphaltenes (from n-C ₇)	0.87	9.29	15.35

(DSC) may be useful to characterize crude oils and their fractions [18, 19]. In the specific case of W/O emulsions, it is important to define the preparation procedure. Emulsions were elaborated in special graduated glass bottles (180 mL) with lids, to prevent any segregation and to obtain a homogeneous mixture. The treated crude, was then placed in a water thermal bath and heated to a temperature that approximates the formation temperature of the geological formation from which the crude oil was obtained (in this case, about 60 °C) during 10 min [7]. A volume of 100 mL of crude oil was measured and introduced into each glass bottle. Afterward, distilled water was added to reach a concentration of 5% (v/v). A continuous vertical movement by hand, of the glass bottle was made for 3 min, to improve macro-stirring of the system—like a bottle test procedure.

It was also important to carry out rigorous sampling, after emulsions' preparation. The sample had to be stable and representative of the entire mixture; a 1-mL syringe was used for this purpose, one droplet was taken and gently deposited on a perfectly clean Al crucible, and this procedure was repeated with samples with 10 and 20% (v/v) content of distilled water.

DSC characterization

When DSC was performed on emulsions, two parameters were of utmost importance: sample volume and scanning rate [7]; the smallest ones are the best. A compromise had to be made, and this normally needs practice and preliminary experiments. Crystallization temperatures of the W/O emulsions were detected by DSC using a Shimadzu DSC-60A with a TA-60WS interface. A calibration procedure was performed using two calibration materials [20] with melting temperatures—one above and the other below temperature range of interest. Water and Indium were used as reference standards. The apparatus was continuously

flushed with nitrogen at 20 mL/min, and an empty crucible was held in the reference cell. Samples weighed between 8 and 22 mg, containing roughly 10^6 droplets of water [11, 21]. The sample weight was limited by the dimension of the emulsion droplet. As a result of this, global information on the sizes of a very large number of droplets, from 5×10^6 to 200×10^6 , depending on droplets size and the volume of the emulsion sample under study, is obtained [8]. All the heating and cooling rates were $\dot{q} = 5^\circ\text{C}/\text{min}$ according to Dalmazzone's recommendations [9, 22]. First, the sample was heated to 30°C and held for 3 min; it was then cooled by using liquid nitrogen up to -60°C , holding it for 3 min and reheating again to 30°C . This was the first cycle. A similar second cycle was performed to analyze the influence of the first cycle regarding the sample's stability, and to corroborate the peak's position. These low-temperature tests are non-destructive; several measurements can be performed by using the same sample, considering that at 30°C , the thermal stability of the crude oil is significant.

Results

The crude oils were first evaluated to determine their main characteristics and properties, as reported in Table 1. All samples consisted of a little content of water and salt, specially the light crude oil. Similar wax contents were also determined for the three petroleum samples. A perfect correlation between the kinematic viscosity and the pour point was observed for all the series of crude oils; the light petroleum, with a reduced viscosity, begins to flow at a low temperature of -45.0°C whereas for the very viscous heavy crude oil, a pour point of -20°C is required to start displacing it. The SARA analysis revealed a saturate content decrease with the API density of the samples. An opposite dependence of the other compound fractions with the API density may be established; specifically apparent in the case of asphaltenes. The highest asphaltene content was detected in super-heavy crude oil. This parameter is very important it is well known that water droplets are stabilized in petroleum mainly by asphaltenes [22–25].

Samples of the three dry crude oils were thoroughly characterized by DSC. The three types of petroleum were submitted to a first cooling cycle, the obtained curves are shown in Fig. 1. Just a reduced water percentage, close to 0.30% in the heavy crude oil was determined from these curves. In the other small samples of light and heavy petroleum, no water was detected.

Afterward, samples of crude oil, dry, and with different contents of emulsified water (5, 10, and 20%) were characterized by DSC. New peaks in the cooling and heating curves were found when water was added—associated to the

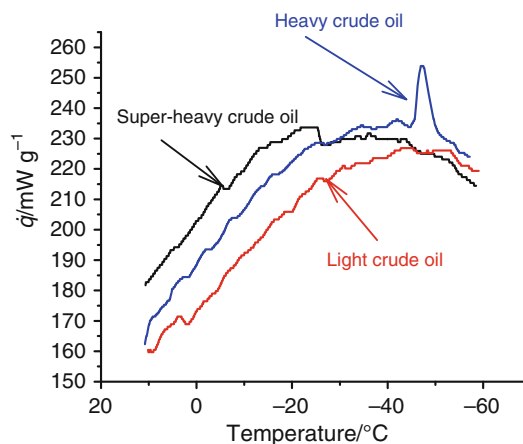


Fig. 1 Curves of light, heavy, and super-heavy crude oils submitted to a first cooling cycle

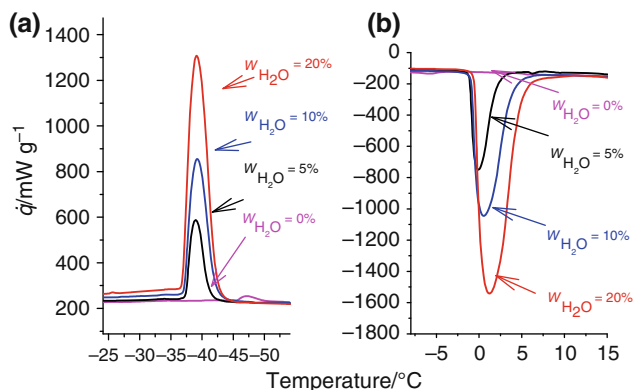


Fig. 2 Curves of a sample of heavy crude oil containing emulsified water at 0, 5, 10, and 20% (w/w) and submitted to a first cycle: **a** cooling and **b** heating

crystallization and fusion of the water droplets in light, heavy, and super-heavy crude oils—as shown in Fig. 2, for the heavy oil.

The curves showed that the superior and the maximum levels in the fusion peak of the W/O emulsions in light, and heavy crude oils were shifted to higher temperatures, when the water content was increased. These signals represent the overlay of several individual Gaussian-like peaks, obtained for each emulsified water content corresponding to each droplet size. The curve of water emulsified in super-heavy crude oil had the maximum at a water content of 10% (w/w) instead. Five similar signals were assigned to crystallization temperatures of W/O emulsions of the three crude oils, and are shown in Fig. 3. It was supposed in this context, that the water minimum crystallization temperature did not exceed -60°C . Therefore, as an example, Clause and Dalmazzone have found crystallization temperatures lower than -45°C with water solutions with

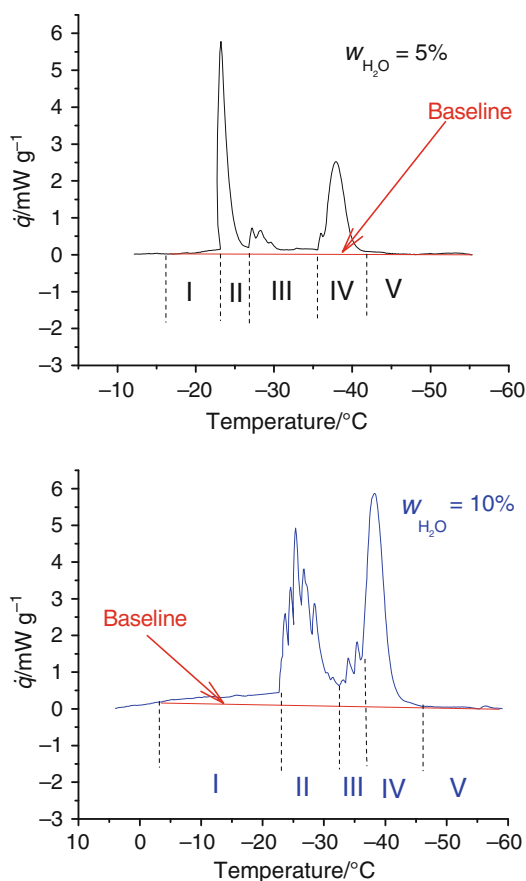


Fig. 3 Assignment of the baseline and different signals (zones) for the super-heavy crude emulsions with 5 and 10% of distilled water at the first cooling cycle

NaCl or urea, up to -82 or -60 °C, respectively [13, 25]. It was considered that crude oil components, such as asphaltenes, resins, and present solids could diminish the crystallization temperature up to -60 °C.

It is important to indicate that the IV signal in Fig. 3, between -36 and -46 °C, was the most regular one, associated to the normal highest crystallization temperature of pure water [26–28]. Furthermore, the regularity of the signals pointed out that the interfacial tension between the water and the three kinds of petroleum was similar in the range of temperature evaluated, enabling the association of a unique drop diameter to the crystallization temperature determined by DSC.

The second cycle measurements had a high influence of the first cycle scanning on the W/O light crude emulsions, producing a shift to higher temperature in the curve. If this shift to higher temperature is associated to a higher drop diameter; then this shift indicates a coalescence of the droplets. In contrast, the second cycle did not even have an influence in respect of the curves in W/O heavy and super heavy crude emulsions.

Discussion

It was considered that the water droplet did not change its diameter during the cooling process, to evaluate the water droplet diameter in the W/O emulsions. Consequently, the difference of pressure between the water droplet and the surrounding oil $\Delta P_{w,o} = P_w - P_o$ changed with the water–oil interfacial tension γ_{wo} in accordance to Laplace equation:

$$\Delta P_{w,o} = \frac{4\gamma_{wo}}{D_d} \tag{1}$$

where D_d is the drop diameter. Because this interfacial tension changes slowly [25], it was considered that the difference of pressure was almost constant, as shown in Fig. 4. An assumption was then made that the temperature obtained in DSC was the equilibrium freezing temperature of water T_{f_2} , given by the Clausius Clapeyron equation [26, 29–31]:

$$\ln\left(\frac{T_{f_2}}{T_{f_1}}\right) = -\frac{\Delta P'_{T_2,T_{f_1}} \Delta V_{m,c}}{\Delta H_{m,f}} \tag{2}$$

where T_{f_1} is the normal freezing temperature of water at 1 atmosphere, say, 273.15 K; $\Delta P'_{T_2,T_{f_1}} = P_{T_{f_2}} - P_{T_{f_1}}$ is the pressure difference between these equilibrium temperatures; $\Delta V_{m,c}$ is the change of molar volume in the crystallization temperature; and $\Delta H_{m,f}$ is the fusion molar enthalpy. The effect of the droplet curvature [17] was not included in this equation. It was considered that when the temperature declined, the cooling rate was so slow that the crystallization temperature of the drop of water was the equilibrium crystallization temperature T_{f_2} , and the pressure at this temperature, $P_{T_{f_2}}$, was equal to the pressure inside this drop P_w :

$$P_w = P_{T_{f_2}} \tag{3}$$

And the drop diameter D_d is finally obtained as follows:

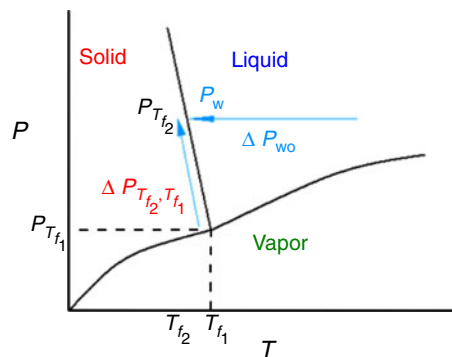


Fig. 4 Water phase diagram of temperature versus pressure showing that the equilibrium crystallization temperature $P_{T_{f_2}}$ equals the pressure of the spherical water drop P_w [34]

$$D_d = \frac{4\gamma_{wo}}{-\frac{\Delta H_{m,f}}{\Delta V_{m,c}} \ln\left(\frac{T_f}{T_i}\right) + P_{Tf_i} - P_o} \quad (4)$$

It is considered that $\Delta H_{m,f}$ does not change with the temperature, although the fusion enthalpy decreases with the decrement of temperature [17, 32–34]. Calculations show that the variation of enthalpy is not important in the statistical analysis of the diameter droplet distribution. Besides, the interfacial tension γ_{wo} was calculated using the equation [35, 36].

$$\gamma_{wo} = \gamma_w + \gamma_o - 2\Phi(\gamma_w\gamma_o)^{1/2} \quad (5)$$

With

$$\Phi = \frac{4V_{m,w}^{1/\beta}V_{m,o}^{1/\beta}}{(V_{m,w}^{1/\beta} + V_{m,o}^{1/\beta})^2} \quad (6)$$

where γ_w and γ_o are the surface tensions of water and oil, respectively; and $V_{m,w}$ and $V_{m,o}$ are the molar volumes of the water and oil, respectively. We have not considered that the surface tension of water γ_w had an asymptotic value close to $-45\text{ }^\circ\text{C}$ as was assumed by Pruppacher [17], with a total crystallization of water at this temperature.

It is important to make it clear that the calculated diameter values of the droplets were in the order of nanometers at a temperature close to $-40\text{ }^\circ\text{C}$, two orders of magnitude less than the values at this temperature found by Dalmazzone [8]. These calculated frozen droplet diameters were approximately of the ice germs, of nanometric size [17, 32, 33], but not of the real frozen droplet diameters. Nevertheless, the values were useful, both for comparing the size distributions between the different W/O emulsions of the crude oil, and finding out in which W/O crude emulsion, the stability changed with the sequential addition of distilled water.

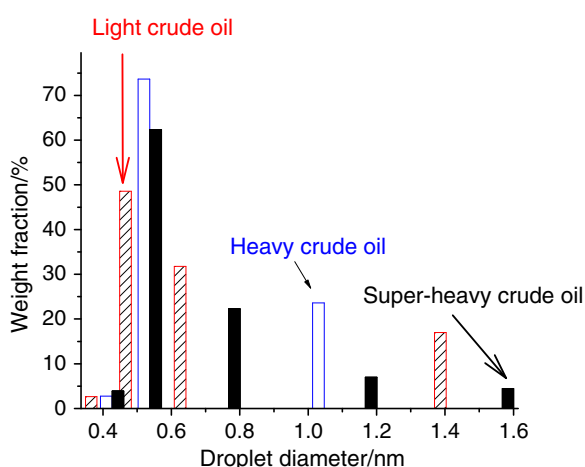


Fig. 5 Diameter drop distribution of emulsified water in light, heavy, and super-heavy oils with 20% of distilled water (w/w)

In Fig. 5, histograms of the diameter distribution versus weight fraction showed that higher percentage of crystallization corresponded to signal IV, in accordance with Dalmazzone [9]. This figure shows the droplet diameter histogram of the crudes with 20% distilled water.

In general, light crude oil showed a decline of the smallest droplet weight fraction and, at the same time, an increase in the proportion of the larger droplets with the increment of water content. Thus, the heavy crude oil had only a small coalescence with the increment of water content. The super-heavy W/O emulsion showed two phenomena: an increase of the smallest droplets and an increment of larger droplets (Fig. 6). The Z-average diameter D_{dz} given by Collins [37] was determined to analyze the statistics of the water drop diameter:

$$D_{dz} = \frac{\sum N_i D_{di}^3}{\sum N_i D_{di}^2} = \frac{\sum w_i D_{di}^2}{\sum w_i D_{di}} \quad (7)$$

It was found that the emulsions prepared in light and heavy crude oils showed the same D_{dz} with 5 and 10% of distilled water. When the percentage of distilled water was 20%, the light crude oil emulsions showed a higher coalescence than those formed in heavy crude oils. Besides, the super-heavy crude showed almost the same average diameter D_{dz} in each W/O emulsion, and with 5 and 10% of distilled water, its diameter values D_{dz} were higher than the other oils.

In order to analyze the stability in the emulsions through kinetic parameters, the nucleation rate J was calculated as per the following equation [38]:

$$J = \frac{1}{v_g \Delta t} \ln\left(\frac{A_t}{A_{(t+\Delta t)}}\right) \quad (8)$$

where v_g is the volume of one drop; Δt is the time increment between the experimental measurements; A_t is the area of

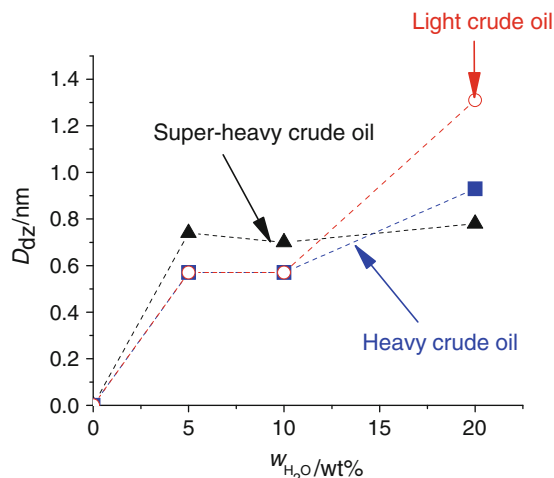


Fig. 6 Volume average drop diameter D_{dz} of light, heavy, and super-heavy crude oils emulsified with 5, 10, and 20% of distilled water

the curve between the time of total freezing; and t is the time of the measurement; $A_{(t+\Delta t)}$ is the area between the time of total freezing, and the next measurement at time $t + \Delta t$. The values of J are in the order of 10^{15} – 10^{22} drops/cm³/s. It was found in the W/O emulsions of light crude oil that the nucleation rate J with 10% of distilled water was higher than the emulsions with 5 and 20% of distilled water. On the other hand, the W/O emulsions of the heavy crude oil had a higher instability with 5% of water content compared to the 10 and 20% emulsions, as shown in Fig. 7. A temperature close to -10 °C was also found with a local maximum in J , and a temperature close to 50 °C with a local minimum in J in this 5% heavy crude oil emulsion. Regarding the super-heavy crude oil emulsions, they presented higher maxima of J at lower temperatures than the other crude oil emulsions with the same content of distilled water.

A second cycle of heating and cooling was performed to clarify whether the first cooling up to -60 °C and the first heating of crude oils affected their emulsion stability. It was found that the droplet size distribution did not appreciably change in the heavy and super-heavy crude oil emulsions; while the size distribution was displaced to higher diameters in the light crude oil emulsion. Furthermore, at 20% of distilled water, the highest frequency in solidification was not the signal IV, but a lower diameter contradicting Dalmazzone’s statement. This behavior is shown in Fig. 8.

The nucleation rate J was also calculated for the first and second cooling cycles, for light crude oil emulsified with 20% of distilled water, and two maxima were determined for the second cooling cycle, instead of a single maximum as in the first cycle (see Fig. 9). It could thus be stated, with the last two figures, that the light crude oil emulsion had a strong instability regarding temperature. It is also important to add that the curves shown in the cooling cycles, in

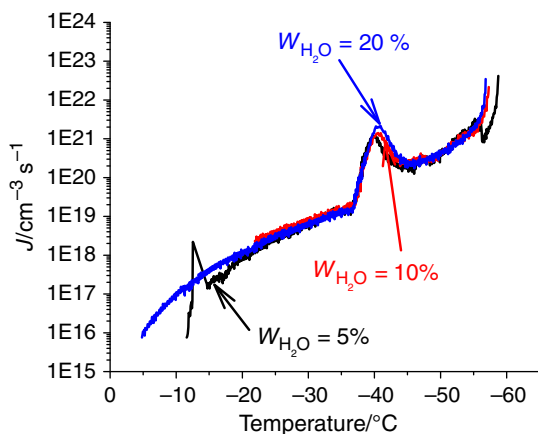


Fig. 7 Nucleation rate (J) of water droplets dispersed in heavy crude oil as a function of the supercooling temperature (5, 10, and 20% of distilled water (w/w))

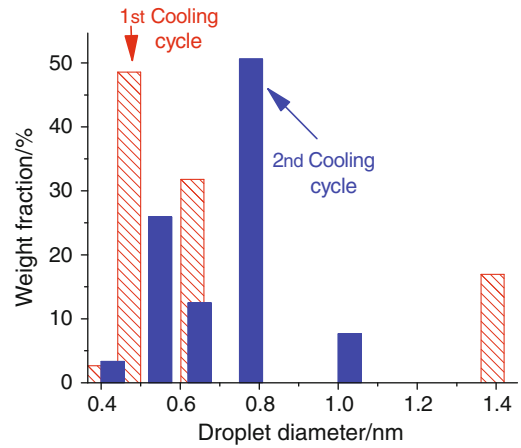


Fig. 8 Effect of the first cooling cycle from 30 to -60 °C and first heating cycle from -60 to 30 °C over the second cooling cycle from 30 to -60 °C of a W/O emulsion of a light crude oil with a 20% distilled water content

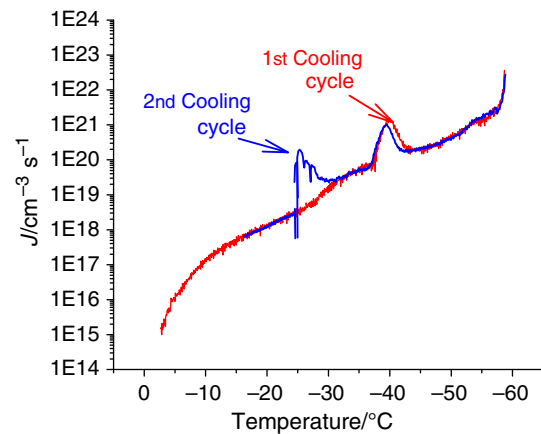


Fig. 9 Nucleation rate (J) versus temperature for light crude oil emulsified with 20% of distilled water (w/w) during the first and second cooling cycles

specific zones, showed an increase of temperature [9, 14], instead of a corresponding decline. This was associated to an extra high change of nucleation rate J , producing a high heating of the sample, and then a rapid decline in the J value, as shown in Fig. 9.

An analysis of the concepts, in which the deduction of this simplified drop diameter assignation is based, shows that it is necessary to add the effect of the curvature in the nucleation of the frozen droplet. If this effect is mentioned and considered based on Pruppacher [17] methodology, then the diameter of the droplet is:

$$D_d = \frac{4V_{m,i}\gamma_{iw}/0.8 + 4V_{m,i}\gamma_{wo}}{(h_{i,1-2} - h_{o,1-2}) \ln\left(\frac{T_f}{T_i}\right)} \tag{9}$$

Here, $V_{m,i}$ is the ice molar volume [39]; γ_{iw} and γ_{ow} are the liquid water–ice and liquid water–oil interfacial

tensions, respectively; $(\overline{h_{i,1-2}} - \overline{h_{o,1-2}})$ is the average difference of enthalpy between the ice and the oil from the crystallization temperature of reference, T_{f1} , as defined above, to the main freezing temperature, T_{f2} , determined by the DSC-measurements. It was supposed that the water drop was surrounded by oil, in the deduction of the last equation, and the ice germ was enclosed by the water drop. It was also considered that in the mean freezing temperature, there was 50% of ice and 50% of water in the droplet, and then the ice diameter was 80% of the total drop diameter. Based on this assumption, it was also found in Eq. 8, that the term $4V_{m,i}\gamma_{iw}/0.8$ had a smaller value than the term $4V_{m,i}\gamma_{wo}$. This agrees with the idea that the interfacial tension γ_{ow} influenced the diameter of the droplet, thus validating Eq. 4. However, there are also experiments, not granting importance to the interfacial tension γ_{ow} in the estimation of the droplet diameter; and of importance for determining the crystallization temperature [40]. Equation 9 gave unreasonable droplet diameters for the super-heavy crude, v_g at -50 °C; due to the high enthalpy value of this crude oil. Because of this, it was inferred that Eq. 4 had a better applicability. It is worth clarifying that Eq. 4 gave results similar to those originally stated by Thomson [17, 41] to determine the germ diameter, but Thomson's following equation is related to ice germs surrounded by liquid water, where only one germ is assigned to one droplet:

$$\ln\left(\frac{T_{f2}}{T_{f1}}\right) = -\frac{4V_{m,i}\gamma_{i,w}}{\Delta H_{m,f}D_{\text{germ}}} \quad (10)$$

where $\overline{\Delta H_{m,f}}$ is the average enthalpy between T_{f1} and T_{f2} ; and D_{germ} is the diameter of the ice germ.

Conclusions

The application of thermodynamics in equilibrium has given the possibility of associating a droplet diameter distribution to the crystallization temperatures detected in DSC curves from different kinds of petroleum containing droplets of emulsified water. With these results, the applicability of analytical formulas, instead of empirical correlations, allows a fast and simple analysis of the main physicochemical parameters of W/O emulsions formed in crude oils. An estimation of the average droplet size and emulsion stability may be performed using DSC measurements and the equations obtained from thermodynamical considerations. In the case of emulsions from three Mexican crude oils, it was found that a super-heavy crude oil exhibited a broad drop size distribution of emulsified water, whereas other petroleum, light and heavy crude oils, presented narrow drop distributions, at different water

contents. It was also found that the greater the water content of emulsified water in super-heavy crude oil, the greater the fraction of smaller droplets. It is considered that the high content of asphaltenes and resins in this crude oil leads to the dispersion of a high amount of water in the shape of tiny drops, constituting a very stable emulsion. Furthermore, the stability of W/O dispersions from light and heavy crude oils decreases with the increase of water content. Along with these results, the application of concepts related to the nucleation kinetics led to the performance of a deeper analysis of the stability of W/O emulsions produced in crude oils.

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