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AN EXPERIMENTAL STUDY ON DETERMINING THE HIGHEST THERMODYNAMIC SOLID-LIQUID EQUILIBRIUM TEMPERATURE FOR WAXY OILS

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Abstract. *Crude oil is a complex mixture of hydrocarbons consisting of paraffins, aromatics, naphthenes, asphaltenes and resins. At low temperatures, the solubility of high molecular weight components in the oil decreases and mainly the n-paraffins tend to precipitate as crystal structures. Many efforts have been made by researchers to determine the highest thermodynamic solid-liquid equilibrium temperature of waxy oils. This temperature is evaluated by means of thermodynamic models or experimental methods. In the majority of the works the metastable zone presented not only on the crystallization but also on the dissolution of crystals has been neglected. In the current work it is proposed a procedure to determine consistently the highest solid-liquid thermodynamic equilibrium temperature of waxy oils by using the results of rheometer and DSC experiments.*

Keywords: *highest solid-liquid thermodynamic equilibrium temperature, supersaturation, rheometry, DSC.*

1. INTRODUCTION

Crude oil is a complex mixture of hydrocarbons, heteroatoms (e.g. N, S, O) and inorganic components as salts, sand and water (Sadeghazad et al. 2000; Venkatesan et al. 2003). The saturate hydrocarbons are known as paraffin. At reservoir conditions, i.e. high temperatures (70 – 150 °C) and pressures (50 – 100 MPa), all the paraffin molecules are dissolved in the oil and this mixture of hydrocarbons is a solution in the liquid phase, at this circumstance the oil behaves as a Newtonian fluid (Pedersen and Rønningsen 2000; Andrade et al. 2015). At low temperatures the solubility of high molecular weight components in the oil is decreased and mainly n-paraffins tend to precipitate out as crystal structures.

Many efforts have been made by researchers to determine the highest thermodynamic solid-liquid equilibrium temperature, $T_{eq,SL}$, of waxy oils. This temperature is determined by means of thermodynamic models (Pedersen et al. 1984; Won 1986; Hansen et al. 1988; Won 1989; Pedersen et al. 1991; Erickson et al. 1993; Coutinho et al. 1996; Zhou et al. 1996; Coutinho and Ruffier-Méray 1997; Coutinho 1998; Ji et al. 2004; Chen and Zhao 2006; Ghanaei et al. 2012; Zhao et al. 2014; Bagherinia et al. 2016; Yang et al. 2016) or by means of different experimental methods (Rønningsen et al. 1991a), such as: Visual Method (Ashbaugh et al. 2002; Bhat and Mehrotra 2004; Tiwary and Mehrotra 2004) as normalized by ASTM (2011), Filter Plugging (FP) (Monger-McClure et al. 1999; Ijeomah et al. 2008), Viscometry (Wardhaugh and Boger 1991; Rønningsen et al. 1991b; Kok et al. 1996; Singh et al. 1999; Ijeomah et al. 2008; Magda et al. 2009), Densitometry (Kruka et al. 1995), Cross Polar Microscopy (CPM) (Rønningsen et al. 1991b; Kok et al. 1996; Tiwary and Mehrotra 2004), Differential Scanning Calorimetry (DSC) (Claudy et al. 1986; Hansen et al. 1991; Gimzewski and Audley 1993; Elsharkawy et al. 2000; Jiang et al. 2001; Oliveira et al. 2012; Mendes et al. 2015; Tarcha et al. 2015; He et al. 2016; Yao et al. 2016), cold finger (Monger-McClure et al. 1999), ultrasonic experiments (Meray et al. 1993), Fourier Transform Infrared (FTIR) energy scattering technique (Monger-McClure et al. 1999) and Near Infrared (NIR) scattering technique (Paso et al. 2009).

Although evident improvements have been achieved not only on the thermodynamic modeling but also on the experimental techniques, a key point has been forgotten or neglected by the majority of the authors. Crystallization is a process where an ordered solid structure is formed from a disordered phase. This process involves two main stages, namely nucleation and crystals growth (Hammami and Raines 1999). It is well known and consolidated, at least in the inorganic chemistry area, that as nucleation is a stochastic process a supercooling (or supersaturation) is needed to the onset of this phenomenon (Mullin 2001). In other words, the temperature in which the first crystal precipitates in the solution, called in the current work as crystallization temperature, T_c, is below the thermodynamic solid-liquid equilibrium temperature. The difference between the solid-liquid equilibrium temperature and the crystallization temperature is define as degree of supercooling, $\Delta T_{\sup}$, (Mullin 2001; Nývlt et al. 2001):

$$\Delta T_{\sup} = T_{eq,SL} - T_c \qquad (1)$$

Considering that during heating solid may also exist in a non-equilibrium condition in the solution (Vehkamäki 2006) and consequently metastable states may occur in either crystallization or dissolution of crystals, this work presents a discussion about how to evaluate consistently the solid-liquid equilibrium temperature of waxy oil. The discussion is based on the results of rheometer and μDSC experiments performed at different rate of change of temperature and calls the attention for metastable regions that exist during the crystallization and dissolution of paraffin. Although not considered in the open literature that deals with waxy oils, these metastable regions may interfere directly in the measurement of the highest solid-liquid equilibrium temperature.

2. EXPERIMENTAL PROCEDURE

The analyses and discussions were conducted with model waxy oils. The model oils were composed by a mineral oil (Sigma Aldrich 330779) and a paraffin wax (Sigma Aldrich 327212). Three different compositions were used 5, 10 and 20 wt% of paraffin in oil. It was used two techniques, named rheometric and μDSC analyses. Model waxy oil samples were prepared by dissolving the paraffin wax in the mineral oil and heating them up in a roller oven to 80 °C within a closed bottle. The samples were then stirred at this temperature for 30 min.

Two techniques used to determine the crystallization and dissolution temperatures are now presented: rheometric and DSC analyses. It is worth noting that the purpose is neither to compare the techniques nor to state which is the more accurate but rather, to use the results to discuss the supercooling during wax crystallization.

2.1 Viscometry tests

It was performed rheometric tests by employing a Haake Mars III (Haake Co., Germany) rotational rheometer that can measure a minimum torque of 5.10^{-8} Nm. The temperature in the rheometer was controlled by a Peltier-thermostatic bath system and it was used a 35 mm diameter parallel-plate geometry with a gap of 0.3 mm and sandblasted surface. Before any test, the model waxy oil sample was completely mixed at 80 °C in the roller oven during 30 minutes. A small amount of material was collected and placed in the rheometer plate at 80 °C by using a syringe. The rotor was then lowered to its measuring position, and the temperature was then kept at 80 °C for 30 min to assure thermal homogenization.

During the test the specimen is cooled to a temperature below the crystallization one and then heated again to the initial temperature, the test is performed at a constant temperature rate. A constant shear rate of 5 s^{-1} was imposed in specimen throughout the rheometric tests. All these parameters of the test were kept constant and only the rate of change of temperature, $\dot{T}$, was changed from one test to another. It were analyzed five different $\dot{T}$: 8.5, 5.0, 1.0, 0.5 and 0.1 K/min. The highest temperature rate used, 8.5 K/min, was limited for the cooling and heating system capacity.

2.2 DSC tests

The calorimetry analyses were performed by employing the SETARAM HP μDSC VIIa differential scanning microcalorimeter. The resolution of the equipment is 2.10^{-8} W, the cells used are made from Hastelloy C276 and have a volume of 1.0 cm^3. In all the experiments, approximately 37 mg of the specimen is loaded in the microcalorimeter cell, the temperature is kept in 80 °C for 5 min, then it is performed a cooling until −10 °C followed by a heating until the initial temperature. Two temperature rates were analyzed: 0.8 and 0.1 K/min.

3. RESULTS AND DISCUSSION

The influence of the temperature rate on the crystallization and dissolution temperature for the model waxy oils is now analyzed.

3.1 Rheometric Analysis

Figure 1(a) shows the viscosity as a function of the temperature for the mineral oil and for model waxy oil with 20 wt% of paraffin and temperature rate of 1.0 K/min. The same result is presented as function of the inverse of the temperature in Figure 1 (b). From the beginning of the test, T= 80 °C, until approximately 40 °C the increase of the viscosity of the waxy oil could be well represented by the Arrhenius fit as can be seen in the Figure 1(b). The Arrhenius fit can represent very well the influence of temperature on the viscosity for Newtonian fluids (Bird et al. 1987). As can be seen, as the pure mineral oil is a Newtonian fluid, the viscosity of this material can be well represented by the fit in all the temperature range. On the other hand, the same behavior is not observed by the waxy oil. During the cooling, at some point crystals precipitate out of the solution and start to affect the measured viscosity of the model oil. From this point forward the Arrhenius fit cannot predict the viscosity behavior of the material, and then the temperature at which the curve slope varies is determined as the crystallization temperature, T_c. It is interesting to note that, because of the wax crystallization, the apparent viscosity of the solution increases from 0.01 to 2.0 Pa.s when the temperature varies only 5 °C, i.e., from 40 to 35 °C. Similar behaviors of the viscosity as a function of temperature were already reported for crude oils (Rønningsen et al. 1991b; Marchesini et al. 2012; Andrade et al. 2015).

At the end of the cooling, the specimen is heated to 80 °C with the same temperature rate. As the temperature increases the wax solubility in the oil increases and the crystals dissolve in the solution, which decreases the apparent viscosity of the model oil. When all the paraffin is dissolved in the solution, the material behaves again as a Newtonian fluid. In the current work, to the rheometric analysis, the first point where the Arrhenius fit was capable for predicting the viscosity behavior during the heating is called as dissolution temperature, T_d.

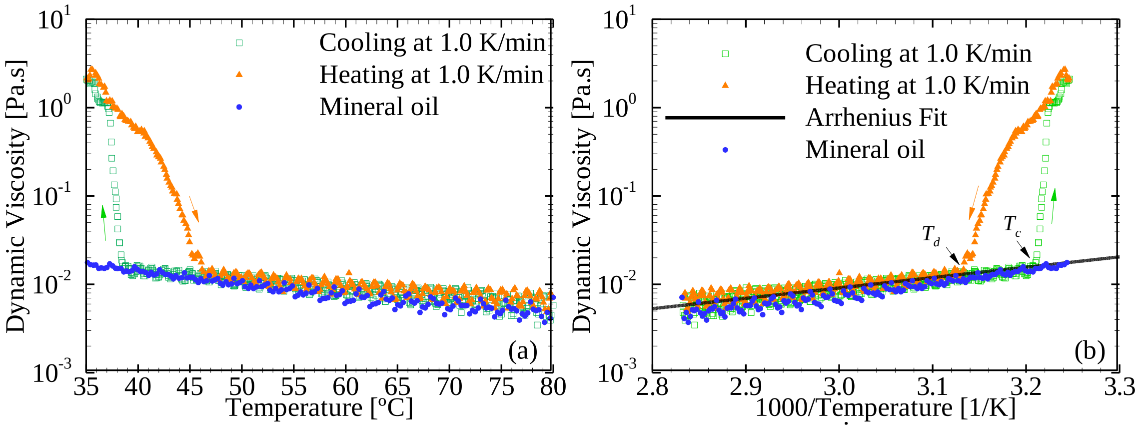

Figure 1. Viscosity of the model waxy oil with 20 wt% of paraffin wax for $\dot{T}$ =1.0 K/min as a function of (a) Temperature and (b) 1000/Temperature. For the Arrhenius fit, η_{ref} (80 °C)= 5.8 mPa.s; $\Delta H/R$ = 2700 K.

3.2 DSC Analysis

The DSC curve of the waxy oil with 20 wt% of paraffin wax is presented in Figure 2. Figure 2(a) presents the heat flux as a function of the temperature during the cooling of the specimen. In this DSC test the cooling rate was kept constant at 0.8 K/min, and the heat flux to maintain this cooling rate was measured.

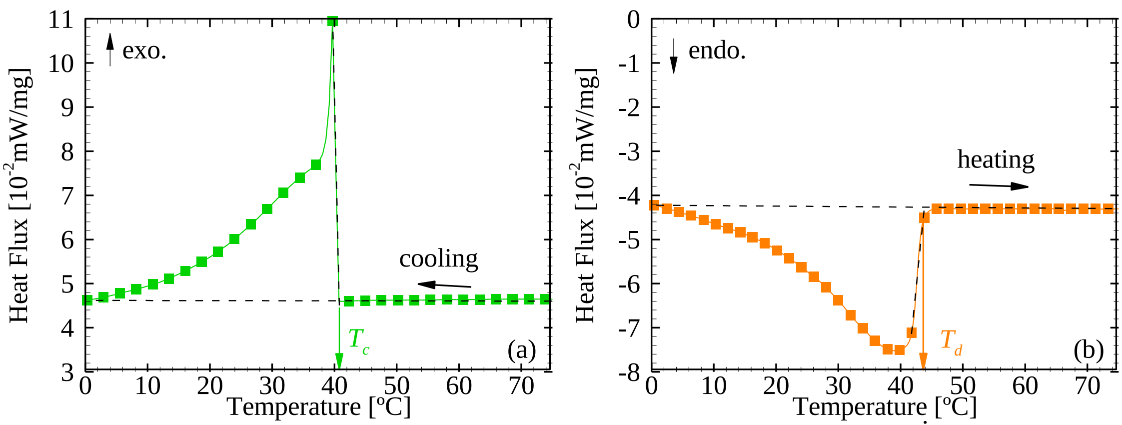

Figure 2. Heat flux in DSC tests of the model waxy oil with 20 wt% of paraffin wax for $\dot{T}$ =0.8 K/min as a function of temperature for (a) cooling and (b) heating process.

As the precipitation of solids in the solution is characterized by a release of energy from the system into the surroundings, when the first crystals precipitate out in the waxy oil an exothermic event takes place. The temperature of the beginning of this exothermic event is called as crystallization temperature, for this case T_c= 40.5 °C as presented by the green arrow. The Figure 2(b) presents the DSC curve for the heating process. The dissolution of paraffin in the oil only takes place if energy is absorbed from the surroundings, because of that in Figure 2(b) it is possible to see that an endothermic event occurs during the heating of the waxy oil. At the end of this event one can conclude that all the paraffins are dissolved and it can be determined the dissolution temperature. As can be seen using the same temperature rate, $\dot{T}$ =8.0 K/min, the dissolution temperature is higher than the crystallization temperature, for this case T_d= 43.9 °C, as presented by the orange arrow.

3.3 Discussion

It is well known that the cooling rate affects the onset temperature for wax crystallization in the waxy oils (Kruka et al. 1995; Monger-McClure et al. 1999; Jiang et al. 2001; Guo et al. 2006). In previous works it were reported that not only the lower the cooling rate the higher the crystallization temperature but also that this dependency is linear (Hammami and Mehrotra 1995b; Paso et al. 2009; Kasumu et al. 2013).

The reason for the influence of the cooling rate on the crystallization temperature resides on the supersaturation. Figure 3**Erro! Fonte de referência não encontrada.** shows a diagram at constant pressure as proposed by Mullin (2001) that facilitates the understanding. A hypothetic solution with a solute concentration represented by the dashed line is cooled from the temperature *A* to *B*. At high temperatures, in the stable region, all the solution is in equilibrium in the liquid state. The point *B* represents the thermodynamic solid-liquid equilibrium temperature or the saturation temperature. On the other hand, it is easy to prove experimentally that the first solid does not precipitate out in the solution exactly in the saturation temperature (Mullin 2001; Nývlt et al. 2001). It is necessary a supercooling or supersaturation for the onset of precipitation. The point *C*, in Figure 3, represents the point in which the first solid precipitates out in the solution. The region between the saturation and the precipitation temperature is commonly named as metastable region. Although the saturation temperature is a thermodynamic property – therefore does not depend on any cooling condition – the precipitation temperature and, consequently, the metastable region width, i.e. the ΔT_{sup} , are affected by many factors as: impurities, solution concentration, mechanical stirring and cooling rate (Mullin 2001; Nývlt et al. 2001). Keeping all the other parameters constants the higher the cooling rate the larger the metastable region width, then the lower the precipitation temperature.

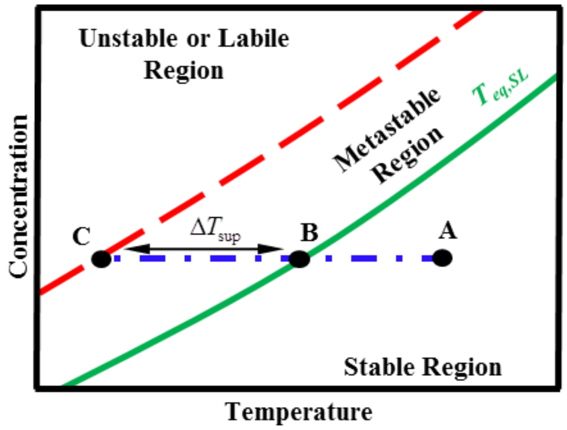

Figure 3. The saturation - supersaturation diagram as proposed by Mullin (2001).

The main reason to the necessity of the supercooling resides on the entropy of the system. The basic principle of entropy in thermodynamics states that the entropy is always maximized in a system. Sloan and Koh (2008) claim that entropy favors disorder over order, then it is required a supersaturation to the paraffins in liquid phase – that are disorderly on a molecular level – rearrange into the crystals that are in the solid phase and molecularly ordered. Then, one can conclude that the solution must reach the metastable region to compensate for the entropy lowering of the system.

Just few works on the petroleum area (Taggart et al. 1996; Bott 1997; Coutinho and Ruffier-Méray 1997; Jones 2002; Azevedo and Teixeira 2003; Bhat and Mehrotra 2004; Tiwary and Mehrotra 2004) recognized the requirement of supersaturation to the first crystal precipitation in solution. Keeping in mind that for the same temperature rate the supercooling is much higher than the superheating for the same material (Hammami and Mehrotra 1995a; Kruka et al. 1995; Bhat and Mehrotra 2004), some authors (Hammami and Mehrotra 1995a; Coutinho and Ruffier-Méray 1997; Bhat and Mehrotra 2004) have proposed a better way to determine the equilibrium thermodynamic temperature. In their works it is proposed that the $T_{eq,SL}$ would be determined not during the cooling but during the heating of the material, promoting the dissolution of the crystals rather than its crystallization, a well-established process in hydrates area (Sloan and Koh 2008).

An interesting discussion was proposed by Taggart et al. (1996) for a pure alkane ($C_{18}H_{38}$). The authors determined the solidification and melt temperatures for different temperature rates. It is showed that even for very slow temperatures rates there was a difference between the solidification and the melt temperatures.

Motivated by the Taggart et al. (1996) discussion, a similar analysis is now proposed for model waxy oils. Figure 4 (a) shows the temperature rate in the y-axis by the temperature in x-axis for the results obtained with the model oil composed with 20 wt% of paraffin wax. The points shown are average values of T_c and T_d obtained from rheometric test results measured three times, and the error bars represent the standard deviation value in each test condition. As already reported in previous work (Hammami and Mehrotra 1995b; Paso et al. 2009) the crystallization temperature is inversely proportional to the temperature rate, the lower the $\dot{T}$ the higher the T_c. The minimum crystallization temperature can be then estimated using the linear trend line and be calculated when $\dot{T}$ =0 K/min, i.e, T_c (at $\dot{T}$ =0 K/min)= 41.3 °C. It is important to say that the correlation coefficient was found to be greater than 0.99.

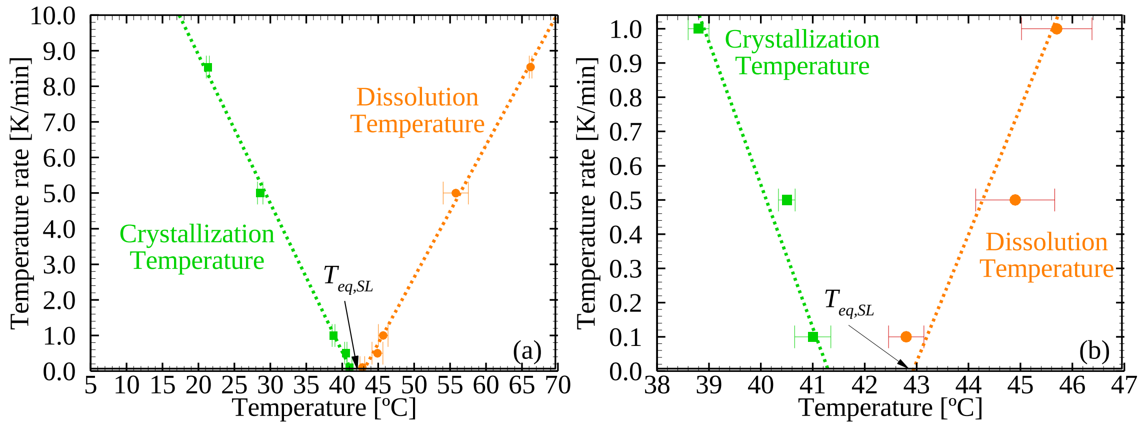

Figure 4. (a) Influence of the temperature rate on the crystallization and dissolution temperatures measured in the rheometric tests with the model oil composed with 20 wt% of paraffin wax. (b) The same results are presented altering the graphic scale to detail the results obtained using the lowest temperature rates.

It is worth noting that not only T_c but also T_d has a linear dependency on the temperature rate. For the last case the lower the $\dot{T}$ the lower the T_d. It can be easily conclude that even the dissolution temperature was affected by the temperature rate. As the solid-liquid equilibrium temperature is a thermodynamic property and cannot be dependent on the conditions of the experiment, it is not possible to use any heating rate to determine the $T_{eq,SL}$ as proposed by some researchers. One can follow the same line of thought adopted elsewhere (Taggart et al. 1996) and assumes that when the heating rate tends to zero, the superheating vanishes and the dissolution temperature would be the best approximation of the thermodynamic solid-liquid equilibrium temperature. Of course that the determined $T_{eq,SL}$ value depends on the precision of the equipment used to determine the dissolution temperatures in the entire range of heating rate analyzed. From the linear trend line presented in Figure 4 (a) it can be concluded that for this model waxy oil using the rheometry technique, $T_{eq,SL}$= T_d (at $\dot{T}$ =0 K/min)= 42.9 °C.

In order to facilitate de visualization, the same results showed in Figure 4(a) are presented reducing the scale of the axes in Figure 4(b). In this figure the three lowest temperature rates are detailed. It is easier to conclude that even for the lowest temperature rate, i.e., 0.1 K/min, the crystallization temperature is not equal the dissolution temperature. One can conclude that, for the parameters used, the minimum metastable region width is obtained when the temperature rate tends to zero, i.e., $\Delta T_{\text{sup,min}}$ = 42.9 – 41.3 = 1.6 °C.

The same experiments were performed to other two model waxy oils. The results of the influence of the temperature rate on T_c and T_d for the model waxy oils with 10 and 5 wt% of paraffin wax are presented, respectively, on Figure 5 (a) and (b). All the tendencies were determined using a linear trend line, the correlations coefficients were greater than 0.99 for the Figure 5(a) and greater than 0.95 for the Figure 5(b). As reported above, it can be determined the minimum crystallization temperature and the $T_{eq,SL}$ for both cases. For the model waxy oil with 10 wt% one can estimate that T_c (at $\dot{T}$ =0 K/min)=34.3 °C, $T_{eq,SL}$ = T_d (at $\dot{T}$ =0 K/min)= 36.0 °C and that the minimum degree of supercooling is $\Delta T_{\text{sup,min}}$ = 1.8 °C For the other case, in which the model oil was formulated with 5 wt% of paraffin wax, T_c (at $\dot{T}$ =0 K/min)= 26.7 °C, $T_{eq,SL}$ = T_d (at $\dot{T}$ =0 K/min)= 32.0 °C and $\Delta T_{\text{sup,min}}$ = 5.3 °C.

It is worth noting that not only the higher the temperature rate the higher the supercooling but also that the lower the wax concentration the higher the metastable region width. As discussed above the lower the saturation temperature, in other words the lower the solute concentration, the higher the supercooling that is necessary to the precipitation of the first crystal in solution (Mullin 2001; Nývlt et al. 2001).

The same analysis was performed with the model oil composed with 20 wt% of paraffin wax using the DSC technique. The crystallization and dissolution temperature for the temperature rates employed in these experiments are presented in Figure 6(a). The points shown are the average values of T_c and T_d obtained from the DSC test results that were repeated twice and the error bars are the standard deviation. As reported above the tests were performed at 0.8

and 0.1 K/min. As can be seen, the same tendency showed by the rheometric results can be observed by the DSC measurements, i.e., the higher the $\dot{T}$ the lower the T_c and the higher the T_d. From the linear trend line presented in Figure 6(a) it can be concluded that for this model waxy oil using the DSC technique, T_c (at $\dot{T}$ =0 K/min)= 40.8°C, $T_{eq,SL} = T_d$ (at $\dot{T}$ =0 K/min)= 42.6 °C and then $\Delta T_{\sup,\min}$ = 1.8 °C.

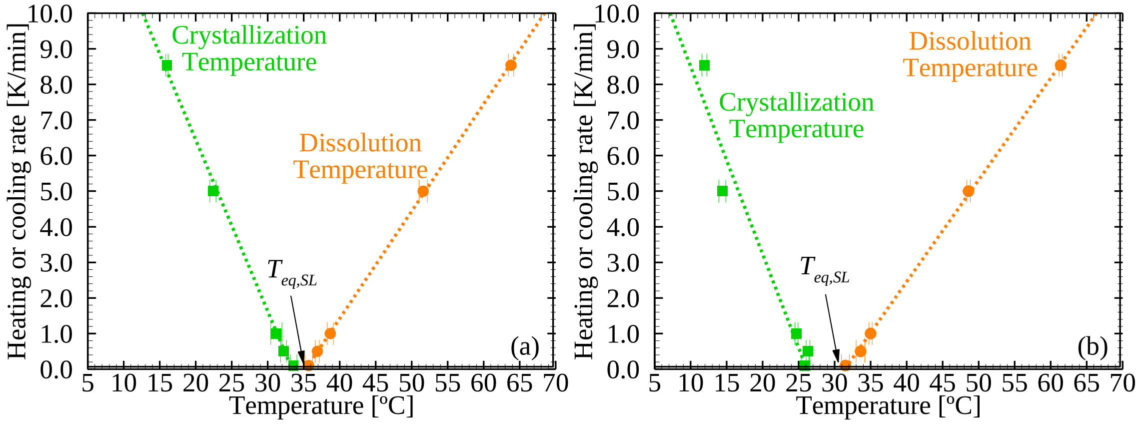

Figure 5. Influence of the temperature rate on the crystallization and dissolution temperatures measured in the rheometric tests with the model oils composed with (a) 10 wt% and (b) 5 wt% of paraffin wax.

In order to compare the rheometric and the DSC measurements, Figure 6(b) presents the results obtained in the range of temperature rate from 0.1 to 1.0 K/min using both techniques. One can see that for this specific waxy oil both techniques obtained very similar values for $\dot{T}$ = 0.1 K/min. With the exception of the crystallization temperature at 0.5 K/min obtained with the rheometric experiment that is well represented by the dashed trend line, at higher temperature rates the results obtained with different techniques presents a small divergence. On the other hand, the $T_{eq,SL}$ determined when the temperature rate tends to zero is very similar when both techniques are analyzed. As presented above using the rheometric results $T_{eq,SL} = T_d$ (at $\dot{T}$ =0 K/min)= 42.9 °C and for the DSC measurements $T_{eq,SL} = T_d$ (at $\dot{T}$ =0 K/min)= 42.6 °C.

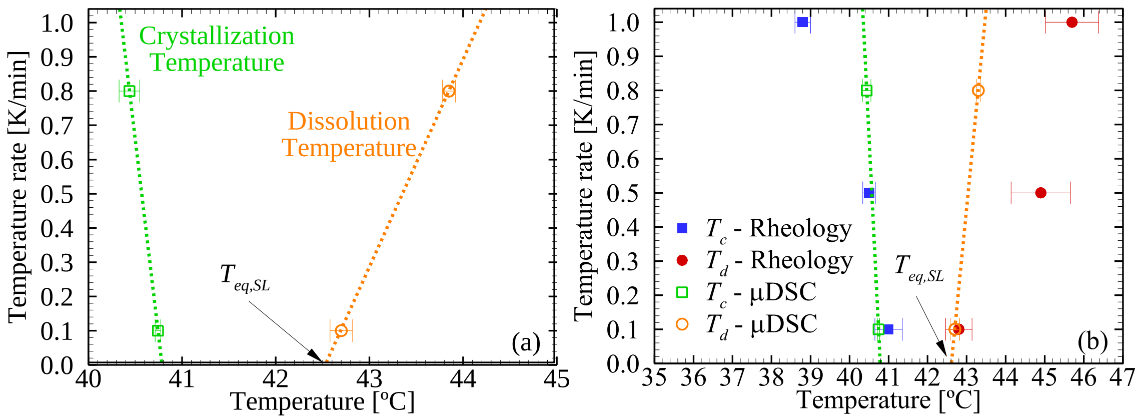

Figure 6. Influence of the temperature rate on the crystallization and dissolution temperatures of the model oil composed with 20 wt% of paraffin wax measured in the (a) DSC tests and (b) DSC and rheometric experiments.

It can be seen that the same tendency observed by a pure alkane as presented by Taggart et al. (1996) was also noted for waxy oils in the current work. Then, one can conclude that the most coherent way to determine the thermodynamic solid-liquid equilibrium temperature is by means of heating the material, as discussed in a recent work (Andrade et al. 2017). In other words, to overcome the supercooling issue, one has to dissolve the crystals and determine the temperature in which the last crystal was dissolved in the solution. When the heating rate is low enough, the dissolution temperature would be the best approximation of the saturation temperature. As advocated by some authors the rheometry is not the most adequate equipment to determine precisely neither the onset of the crystallization (Rønningsen et al. 1991b; Marchesini et al. 2012) nor the dissolution temperature (Marchesini et al. 2012). But, the main goal of the current discussion is just to call attention for the importance of the supercooling on the crystallization and of the superheating on the dissolution of wax in waxy oils. As concluded by means of rheometric and DSC measurements, it is necessary to take in account the supersaturation in precipitation and dissolution process and to keep in mind that the crystallization temperature, i.e., the temperature in which the first crystal precipitates out in the solution, is not the thermodynamic solid-liquid equilibrium temperature. The $T_{eq,SL}$ is more coherently determined by means of the dissolution temperature when the rate of change of temperature tends to zero.

4. CONCLUSIONS

Wax precipitation is a huge problem in production and transportation of crude oil. Many efforts have been made to determine the thermodynamic solid-liquid equilibrium temperature. In the current work, by means of rheometric and DSC experiments, it was discussed about the importance of the metastable regions present not only on the wax crystallization but also on the dissolution oj wax crystals. It was proposed a better way to determine the thermodynamic solid-liquid equilibrium temperature. The main conclusions of the paper might be summarized as:

i. A supercooling is absolutely necessary to the onset of wax precipitation in waxy oils;
ii. Not only the solute concentration but also the rate of change of temperature affects the metastable region width, in other words, $\dot{T}$ affects the degree of supersaturation, ΔT_{sup};
iii. The higher the cooling rate the higher the degree of the supercooling, i.e., the lower the crystallization temperature;
iv. The lower the solute concentration the higher the degree of supercooling;
v. The degree of supercooling during the wax precipitation is never null, in other words, even when the cooling rate tends to zero the degree of supercooling tends to a non-zero value. On the other hand, in the dissolution of the wax crystals the superheating vanishes when the heating rate is low enough;
vi. The temperature in which the first wax crystal precipitates out in solution is called as crystallization temperature, T_c, and because of the supercooling issue its temperature is not the thermodynamic solid-liquid equilibrium temperature;
vii. The thermodynamic solid-liquid equilibrium temperature can only be experimentally determined by heating the material with a low enough heating rate. In other words, the saturation temperature is equal the dissolution temperature when the rate of change of temperature tends to zero.

5. ACKNOWLEDGEMENTS

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