THE INFLUENCE OF THE SUPERCOOLING ON THE MECHANICAL PROPERTIES AND CRYSTAL MORPHOLOGY OF WAXY OILS

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Abstract. *Waxy 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 is decreased and mainly the n-paraffins tend to precipitate as crystal structures. These crystals not only provide a non-Newtonian behavior to the fluid but also tend to deposit in the inner surface of pipelines and are responsible for the gelation of the oil when the flow is interrupted. Crystallization is the process where an ordered solid structure is formed from a disordered phase. This process involves two main stages, namely nucleation and crystals growth. As paraffins nucleation is a stochastic process, a supercooling is needed to the onset of this phenomenon. In other words, it could be not possible to occur the precipitation of crystals exactly in the solid-liquid equilibrium thermodynamic temperature, namely in petroleum area as Wax Appearance Temperature – WAT. Therefore, during the cooling it is required that the fluid reaches a certain temperature, below the WAT, to initiate the nucleation process. The difference between the WAT and the crystallization temperature is named as degree of supercooling. In this work the influence of the cooling rate on the supercooling is investigated. The supercooling is related to mechanical properties of waxy crude oils and to the morphology of wax crystals. The analysis is conducted by means of rheometric tests. It can be anticipated that it is possible to associate the degree of supercooling with the mechanical properties and with the crystal morphology of waxy oils.*

Keywords*: waxy Oil, crystallization, supercooling, crystal morphology, mechanical properties*

1. INTRODUCTION

Waxy crude oil is a complex mixture of hydrocarbons, heteroatoms (e.g. N, S, O) and inorganic components as salts, sand and water (Zílio and Pinto, 2002; Vieira, 2008; Santos, 2009). More than 90% of the oil can be composed by hydrocarbons (Zílio and Pinto, 2002) that can be divided in four major fractions: saturates, aromatics, resins and asphaltenes (SARA) (Maqbool et al., 2011; Oliveira et al., 2012; Ilyin et al., 2016). At high temperatures this mixture of hydrocarbons is a solution in the liquid phase (the oil) (Venkatesan et al., 2005). At low temperatures the solubility of high molecular weight components in the oil is decreased and mainly n-paraffins tend to precipitate as crystal structures. These crystals not only provide a non-Newtonian behavior to the fluid (Marchesini et al., 2012; Andrade et al., 2015b) with a variety of features as pseudoplasticity, elasticity and time-dependency (Ding et al., 2006; Tarcha et al., 2015) but also tend to deposit in the inner surface of pipelines (Guozhong and Gang, 2010; Aiyejina et al., 2011) and are responsible for the gelation of the oil when the flow is interrupted (Wardhaugh and Boger, 1987; Oliveira et al., 2012). It is worth mentioning that only 2wt% of crystals is enough to gel waxy oils (Kané et al., 2003; Aiyejina et al., 2011; Paso et al., 2014). As in many cases the subsea oil pipelines lay down over the ocean floor at temperature as low as 4 °C, during the flow the oil loses heat to the surrounding water (Azevedo and Teixeira, 2003) and precipitation of wax crystal becomes usual during transportation of crude oils in offshore productions. In this scenario, when the flow is interrupted for pipeline maintenance, gelation takes place and pump pressures much larger than the usual steady-state pressure are required to break down the gel structure and to start-up the flow (Jemmett et al., 2013; Mortazavi-Manesh and Shaw, 2014). If the mechanical properties of the waxy crude oil at low temperatures were not very well determined and the restart problem was not well calculated, such high pressures can lead to overestimation of pipe dimensions, making the project unfeasible (Oliveira and Negrão, 2015).

During the cooling of a waxy oil the paraffin solubility limit can be reached. In this point it is determined the equilibrium solid-liquid thermodynamic temperature, namely in petroleum area as the Wax Appearance Temperature (WAT) (Venkatesan et al., 2003). Many efforts have been made by researchers to modeling the solid-liquid thermodynamic equilibrium and to determine the WAT of waxy oils (Pedersen et al., 1984, 1991; Won, 1989, 1986; Hansen et al., 1988; Erickson et al., 1993; Zhou et al., 1996; Coutinho et al., 1996; Coutinho and Ruffier-Méray, 1997; Coutinho, 1998; Chen and Zhao, 2006; Ghanaei et al., 2012; Zhao et al., 2014). The general solid-liquid equilibrium equation is well established and is based in the thermodynamic condition that the fugacities of each component "*i*" in solution are identical in solid and liquid phases, resulting in the following equation (Prausnitz et al., 1986):

$$K_i^{SL} = \frac{\gamma_i^L}{\gamma_i^S}\exp\left[\frac{\Delta H_i^F}{RT}\left(1-\frac{T}{T_i^F}\right)+\frac{\Delta C_{p,i}^{SL}}{R}\left(1-\frac{T_i^F}{T}+\ln\frac{T_i^F}{T}\right)+\int_0^P\frac{\left(V_i^L-V_i^S\right)dP}{RT}\right] \qquad (1)$$

where K_i^{SL} is solid-liquid equilibrium constant, γ_i is the activity coefficient, V_i is the volume of component "*i*", S and L superscripts indicate, respectively, the solid and liquid phase, ΔH_i^F and T_i^F are, respectively, the enthalpy and temperature of fusion, $\Delta C_{p,i}^{SL}$ is the difference between the heat capacities of the component "*i*" in the liquid and solid states, *R* is the gas constant and *T* the equilibrium temperature.

Many assumptions have been made to determine the solid-liquid equilibrium of waxy oils. Some authors say that $\Delta C_{p,i}^{SL}=0$ (Won, 1986; Erickson et al., 1993; Coutinho and Ruffier-Méray, 1997), and in some cases the decrease in component volume due to phase transition is disregarded (Pedersen et al., 1991). The liquid phase is assumed in some cases to be an ideal solution ($\gamma_i^L=1$) (Ghanaei et al., 2012) as well as the assumption that $\gamma_i^S=1$ is adopted by some authors (Hansen et al., 1988). The regular solution is used in many works (Won, 1986, 1989; Pedersen et al., 1991; Erickson et al., 1993; Chen and Zhao, 2006) to take the non-idealities of the liquid and solid phases into account. Beyond that assumptions the liquid phase activity coefficient was also determined by Flory-Huggins model (Hansen et al., 1988), by Flory free-volume equation added to a UNIFAC residual term (Coutinho and Stenby, 1996) and by Flory free-volume model (Zhao et al., 2014). The solid phase non-ideality was also considered by Wilson equation (Coutinho and Stenby, 1996) and by UNIQUAC model (Coutinho, 1998; Ghanaei et al., 2012; Zhao et al., 2014). Although some models are better than others in many comparisons, there is not a model that is capable to predict the equilibrium temperature of any waxy oils. The differences between experimental and calculated WAT are generally higher than 2 K and the crystals mass fraction below the equilibrium temperature is qualitatively well represented.

The main idea of the thermodynamic equilibrium models is to determine the WAT and the solid mass fraction at low temperatures. With such information it is possible to project all the equipment and the production and/or transportation process, furthermore one can predict when the paraffin deposition or gelation becomes a real problem in the oil pipelines.

On the other hand, the experimental methods to determine the WAT of waxy oil are not well consolidated. Rønningsen et al. (1991) compared the three more usual methods namely microscopy, differential scanning calorimetry and viscometry. The authors concluded that microscopy is the best method to determine the WAT. In contrast, Kok et al. (1996), using the same three techniques, claimed that the best method to determine the wax appearance temperature depends on the solution composition. Although in a recent work Marchesini et al. (2012) have made an interesting discussion saying that the temperature determined by viscometry/rheometry was not the WAT – because when the first crystal appears in the solution it is too small that does not change the oil viscosity – a key point has been forgotten or neglected by many authors.

Crystallization is the 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, at least in the inorganic area, that as nucleation is a stochastic process a supercooling is needed to the onset of this phenomenon (Stefanescu, 1988; Mullin, 2001; Nývlt et al., 2001). In other words, it could not be possible the crystals precipitation occurs exactly in the solid-liquid equilibrium thermodynamic temperature. Therefore, during the cooling it is required that the solution reaches a certain temperature, below the WAT, to initiate the nucleation process. The difference between the WAT and the crystallization temperature is called as degree of supercooling. Sloan and Koh (2008) claim that entropy favors disorder over order, as to reach the equilibrium the entropy is maximized the supersaturation is always required in any nucleation process.

Just few works on the petroleum area (Taggart et al., 1996; Bott, 1997; Coutinho and Ruffier-Méray, 1997; Jones, 2002; Azevedo and Teixeira, 2003) recognized the requirement of supercooling to the first crystal precipitation in solution. Keeping the importance of the supersaturation in mind, Coutinho and Ruffier-Méray (1997) proposed that the WAT must be determined during the heating of the oil promoting the dissolution of the crystals rather than its crystallization, a well-established process in hydrates area (Sloan and Koh, 2008).

In the current work is not only proposed a discussion of the best way to determine experimentally the WAT, but also determined the influence of the cooling rate on the supercooling. Lastly, by means of rheometry and microscopy tests, it is shown how the supercooling affects the crystal morphology and the mechanical behavior of waxy oils.

2. MATERIALS AND METHODS

A Brazilian crude oil provided by Petrobras and a model waxy oil were used in the investigation. The model oil is composed by 80wt% of a mineral oil (Sigma Aldrich 330779) and 20wt% of a paraffin wax with a melting point specified by the manufacturer to be between 58 and 62 °C (Sigma Aldrich 327212). The normal alkane carbon distribution of both mineral oil and paraffin wax ca be found elsewhere (Dimitriou, 2013). It was performed rheometric tests by employing two rotational rheometers. TA DHR3 rotational rheometer was used to realize the crude oil tests. This rheometer can measure a minimum torque of 5.10^{-9} Nm and these tests were performed by using a 40 mm diameter parallel-plate geometry with a gap of 1 mm and serrated surface to avoid wall slip (Dimitriou et al., 2011). The temperature in the rheometer was controlled by a Peltier-thermostatic bath system. Haake Mars III (Haake Co., Germany) rotational rheometer, that can measure a minimum torque of 5.10^{-8} Nm, was used to perform the model waxy oil experiments. The Rheoscope, a microscope system with a 20x Lens, 1 µm resolution and Black-and-white 'progressive' scan CCD camera, was coupled in the rheometer to get images of the crystals when the model waxy oil was analyzed. A 60-mm-diameter cone-plate geometry, 1° angle, truncation of 0.105 mm, gap of 0.3 mm and polished surface was used in the model oil tests to reflect the light and facilitate the microscope visualization. The experimental procedure for rheological analysis is showed in Tab. 1.

Table 1. Experimental procedure for rheological analysis of the crude and model oils.

Material Analyzed	Crude Oil	Model Waxy Oil
Rheometer	TA DHR3	Haake Mars III
Rotor type	Serrated parallel-plates, 40 mm diameter, gap of 1 mm	Polished cone-plate, 60 mm diameter and 1°
Highest Temperature [°C]	75	80
Minimum temperature [°C]	4	35
Temperature rate, $\dot{T}$, [K/min]	0.1, 1.0, 5.0, 10.0	0.1, 1.0
Static test	Small Amplitude Oscillatory Test, ω= 0.5 Hz, $\gamma_0 = 10^{-3}$	
Dynamic test	$\dot{\gamma}$ =2 s^{-1}	$\dot{\gamma}$ =10 s^{-1}
Analysis of the cooling rate influence on the gel strength at minimum temperature		
Aging time, t_{ag}, at minimum temperature [min]	120	
Stress loading rate, $\dot{\tau}$, [Pa/min]	50	

3. RESULTS AND DISCUSSION

3.1. Crude oil – Determination of the WAT

As discussed above there are many methods to determine the precipitation and dissolution of crystals in waxy oils. Basically, these phenomena can be determined by means of microscope images, thermal analysis and rheometric tests. Although the discussion in the current work is presented based on the rheological behavior of the waxy oil, the central idea can be expanded to the other methods. Figure 1(a) presents the crude oil viscosity as a function of temperature during a cooling following by a heating ramp with shear rate of 2 s^{-1} and temperature rate of 1.0 K/min. At high temperatures the crude oil shows the typical Arrhenius temperature dependence of Newtonian fluids as can be seen in Fig. 1(b), that shows the same results as a functions of the inverse absolute temperature as proposed by some authors (Rønningsen et al., 1991; Webber, 1999; Marchesini et al., 2012).

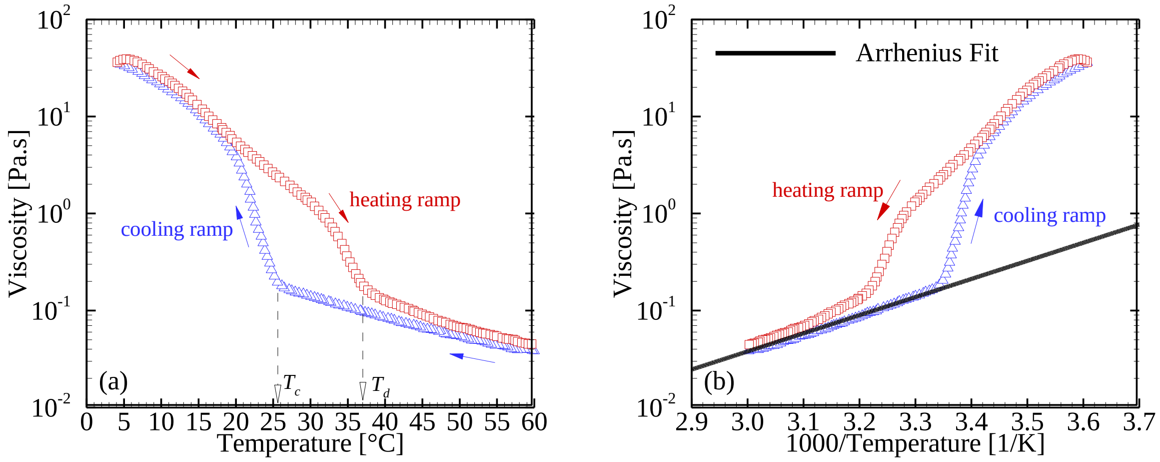

Figure 1. Viscosity of the crude for $\dot{T}$ =1.0 K/min as a function of (a) temperature and (b) 1000/Temperature. For the Arrhenius Fit, η_{ref} (60 °C)= 38.4 mPa.s e $\Delta H/R$ = 4300 K.

As presented by Marchesini et al. (2012) during the cooling of waxy oils the wax precipitation affects the oil viscosity, in this point is determined the crystallization temperature, T_c, as presented in Fig. 1(a). It is worth remembering that this is not the WAT, thermodynamic equilibrium solid-liquid temperature, because the supercooling and, consequently, a metastable condition is always required to the first crystal precipitation. At the end of the cooling a heating ramp was performed with the same $\dot{T}$ and $\dot{\gamma}$. As can be seen in Fig. 1 during the heating the temperature that the crystals do not affect the crude oil viscosity anymore, named dissolution temperature, T_d, is much higher than the crystallization temperature.

As claimed by Hammami and Raines (1999) and explained by Sloan and Koh (2008), using the same rate of temperature change, the superheating during dissolution is substantially lower than the supercooling during crystallization, than one can conclude that T_d is closer to WAT than T_c. Keeping this concept in mind, Taggart et al. (1996) proposed an interesting method to accurately determine the WAT. The authors stated that T_d should be determined using different heating rate, $\dot{T}$, and then, using the tendency of the $\dot{T} \times T_d$ curve, WAT is equal T_d to the case where $\dot{T}=0$ K/min. This analysis is presented in Fig. 2 using two temperature rate, to this crude oil the WAT=33.7 °C. It is worth noting that even when $\dot{T}=0$ K/min the crystallization do not tend to the dissolution temperature. These results corroborate the idea that a metastable zone is always presented in any crystallization process.

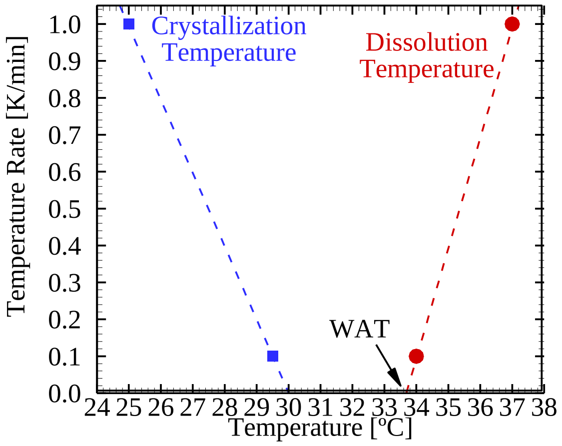

Figure 2. Crystallization and dissolution temperatures as a function of the temperature rate.

3.2. Effect of the supercooling

The results presented in this current section were performed under a static cooling rate, the tests were repeated three times to each experimental condition and all other parameters were maintained constant as presented in Tab. 1. Figure 3(a) shows the influence of the cooling rate on both crystallization and gelation temperatures, T_c and T_g. For these tests the crystallization temperature is determined when the wax precipitation affects the dynamic moduli behavior and T_g is the temperature in which G'-G'' crossover takes place as already explained elsewhere (Andrade et al., 2015b). The points shown are average values and the error bars represent the maximum and minimum values in each test condition. One can note that the higher the cooling rate the lower the crystallization temperature and consequently, defining the supercooling as $\Delta T_{\sup} = T_c - WAT$, the higher the supercooling. A similar behavior is presented by the gelation temperature. It is important to emphasize that T_g varied from 19 to 9 °C when the cooling rate raised from 0.1 to 10 K/min.

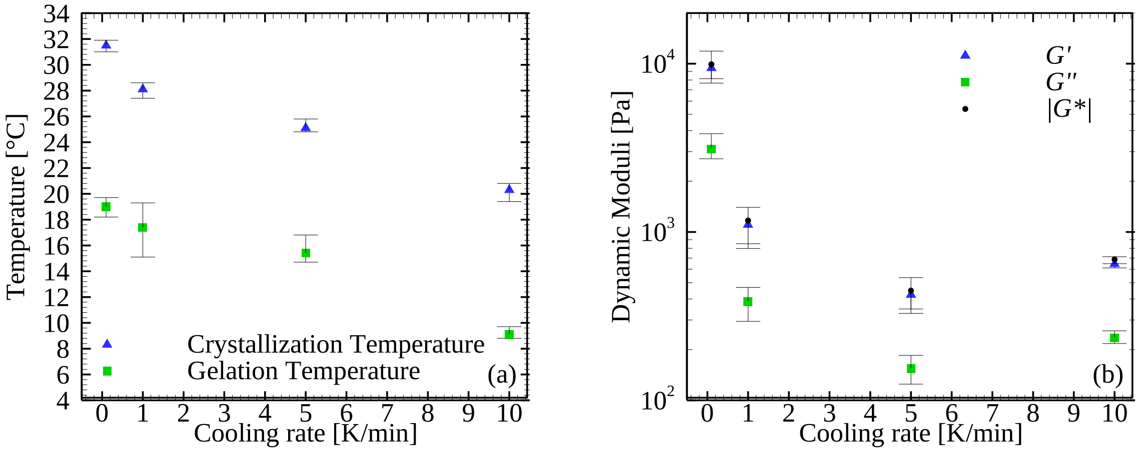

Figure 3. Influence of the cooling rate on the (a) crystallization and gelation temperatures and (b) dynamic moduli.

After the cooling the specimen was aged during 2 hours; in a recent work (Andrade et al., 2015a) it was presented that this is an enough time to material reach the fully structure state. Figure 3(b) presents the dynamic moduli measured at 4 °C after the aging time. As can be seen, in all the cases G' is in the same order of $|G^*|$ which indicates predominant elastic behavior. It is showed that from 0.1 to 5 K/min the higher the $\dot{T}$ the lower the dynamic moduli and a surprising behavior was presented to $\dot{T}$ =10 K/min in which the dynamic moduli are slightly higher than $\dot{T}$ =5 K/min.

The material yield stress was determined performing a stress loading rate test after the 2h aging time. Figure 4(a) presents yield stress as a function of the cooling rate. One can see that the dynamic moduli and yield stress dependence on the cooling rate are quite similar. In this last case, it can be concluded that the yield stress at 5 and 10 K/min conditions are of the same order of magnitude.

Figure 4(b) shows more clearly the influence of the cooling rate on the supercooling, it can be seen that this relation is roughly linear. In the open literature (Mullin, 2001; Nývlt et al., 2001) it is claimed that the higher the supercooling (in other words, the lower the crystallization temperature) the smaller the crystals length. Figure 5 shows the influence of the supercooling on the yield stress, τ_0, of this specific crude oil. One can see that τ_0 is inversely proportional to supercooling as present by the trendline.

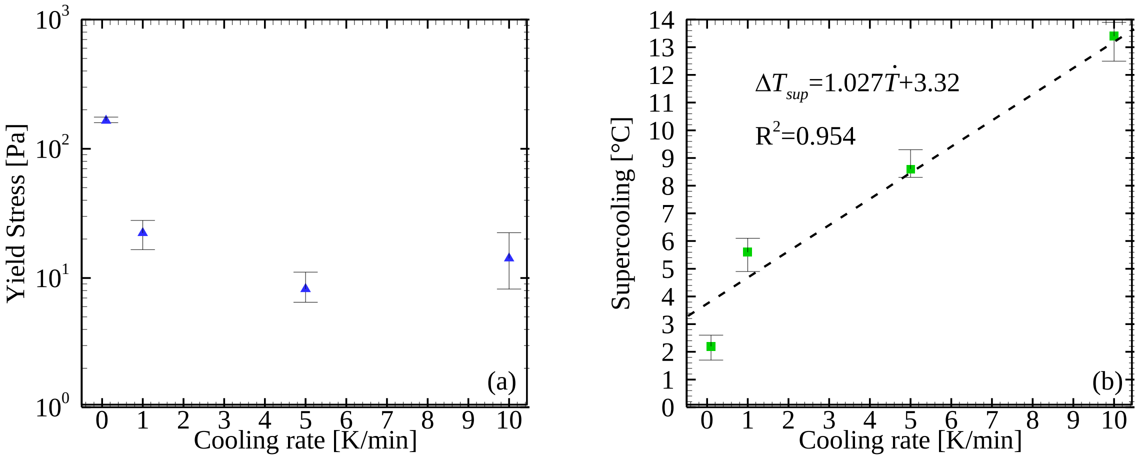

Figure 4. (a) Yield stress as a function of the cooling rate and (b) relation between supercooling and cooling rate.

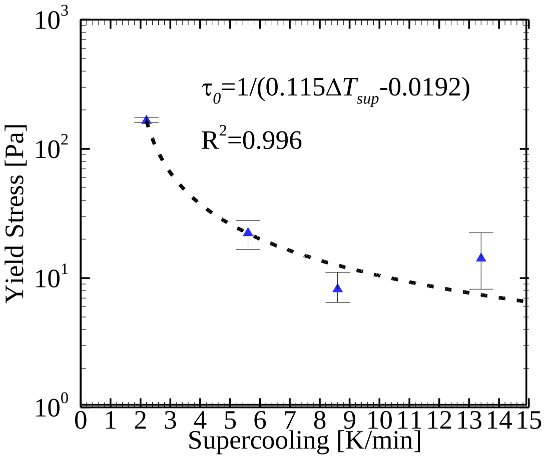

Figure 5. Yield stress of the crude oil as function of the supercooling.

3.3. Model Waxy oil analysis

Some tests were performed with the model waxy oil to correlate the mechanical behavior to crystal morphology. The model oil is transparent above the WAT and them it is possible to visualize the crystals using the Rheoscope system. First of all, it were performed the same tests already discussed to show that the mechanical behavior of this material is similar to the crude oil. Figure 6(a) shows the comparison between the mineral oil (330779) and the model waxy oil viscosity as a function of temperature. As can be seen, as well as the crude oil, due to precipitation of crystals in a certain temperature the model waxy oil viscosity diverges from the Newtonian behavior. The influence of the cooling rate on the crystallization and dissolution temperatures is presented in Fig. 6 (b). Using the same methodology showed in Section 3.1 the WAT=41.4 °C.

Static cooling with two different $\dot{T}$ were performed to visualize the influence of the supercooling on the crystal length. Figure 7(a) and (b) present the crystals morphology after 2 h of aging time at 35 °C for, respectively, $\dot{T}$ =1.0 and

0.1 K/min. One can see that in both case the crystals presents needle-like structure as reported by some authors (Webber, 1999; Venkatesan et al., 2005; Dimitriou et al., 2011). In the first case, ΔT_{sup} =0.9°C, crystal length, L_c, is the order of 50 μm and τ_0= 80 Pa. In the last one, ΔT_{sup} =0.9°C, L_c is the order of 100 μm and τ_0= 150 Pa. It is possible to conclude that, as already claimed above, the higher the supercooling the smaller the crystals and the lower the gel strength. It is known that the action of the van der Walls forces is responsible for attractive interaction among the crystals (Abdallah and Weiss, 2000; Lopes-da-Silva and Coutinho, 2007; Mendes, 2015) and that possibly the crystal roughness interferes in the gel strength of waxy oils (Imai et al., 2001), but the knowledge of how and why the crystal length affects the waxy oil gel strength needs to be improved.

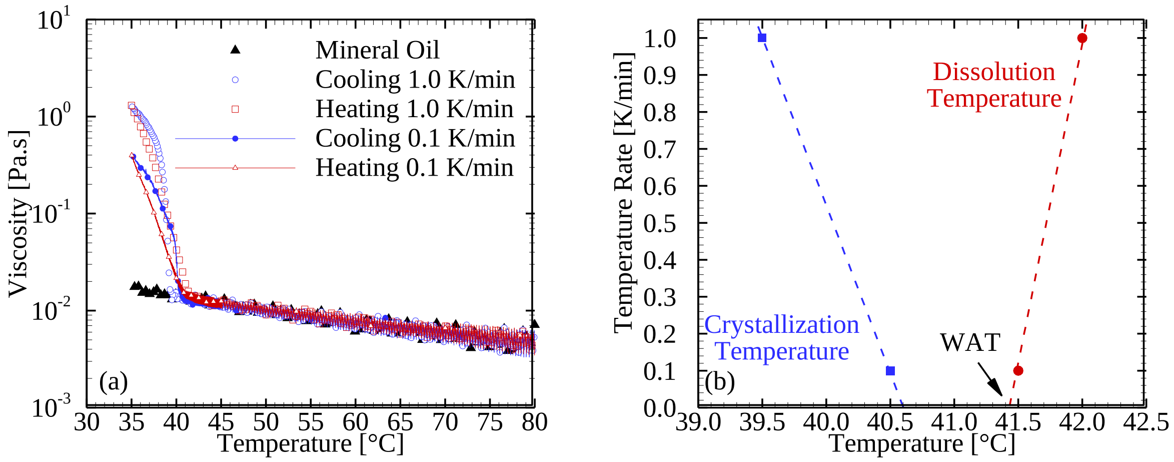

Figure 6. (a) Viscosity of the mineral oil and model waxy oil for $\dot{T}$ =0.1 and1.0 K/min as a function of temperature and (b) Crystallization and dissolution temperatures as a function of the $\dot{T}$. The WAT (at $\dot{T}$ =0 K/min) was 41.4 °C.

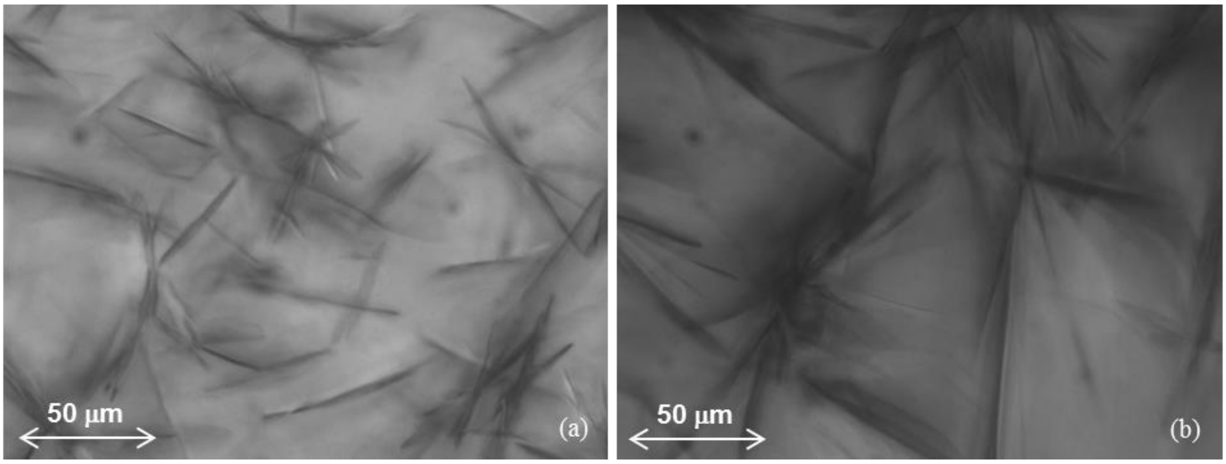

Figure 7. Wax crystals images after static cooling and 2 hour of aging time at 35 °C with (a) 1.0 and (b) 0.1 K/min.

4. CONCLUSIONS

Thermal history has a great influence on the gel strength of waxy crude oil at low temperatures. In the current work it was analyzed the influence of the cooling rate on the gel strength of the material. The main results are summarized as:

1) During the cooling the crystallization does not occur exactly in the equilibrium thermodynamic temperature (WAT). A supercooling is always required in any nucleation process.
2) The WAT, the material thermodynamic property, must be determined during the heating of the oil promoting the dissolution of the crystals rather than its crystallization.
3) The metastable zone width depends on the test cooling rate. The higher the cooling rate the higher the supercooling.
4) The higher the supercooling the smaller the crystals length, even after long aging time.
5) It is possible to correlate the supercooling and the rheological properties of waxy oils.
6) The higher the supercooling the lower the material gel strength.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

Abdallah, D.J., Weiss, R.G., 2000. n -Alkanes Gel n -Alkanes (and Many Other Organic Liquids). Langmuir 16, 352–355. doi:10.1021/la990795r

Aiyejina, A., Chakrabarti, D.P., Pilgrim, A., Sastry, M.K.S., 2011. Wax formation in oil pipelines: A critical review. Int. J. Multiph. Flow 37, 671–694. doi:10.1016/j.ijmultiphaseflow.2011.02.007

Andrade, D.E.V., Baggio, S.C.F., Balvedi, G.A.S., Franco, A.T., Negrão, C.O.R., 2015a. The influence of the thermal history on the mechanical behavior of waxy crude oil, in: 23rd ABCM International Congress of Mechanical Engineering - COBEM.

Andrade, D.E.V., Cruz, A.C.B., Franco, A.T., Negrão, C.O.R., 2015b. Influence of the initial cooling temperature on the gelation and yield stress of waxy crude oils. Rheol. Acta 54, 149–157. doi:10.1007/s00397-014-0812-0

Azevedo, L.F.A., Teixeira, A.M., 2003. A Critical Review of the Modeling of Wax Deposition Mechanisms. Pet. Sci. Technol. 21, 393–408. doi:10.1081/LFT-120018528

Bott, T.R., 1997. Aspects of crystallization fouling. Exp. Therm. Fluid Sci. 14, 356–360. doi:10.1016/S0894-1777(96)00137-9

Chen, W., Zhao, Z., 2006. Thermodynamic Modeling of Wax Precipitation in Crude Oils. Chinese J. Chem. Eng. 14, 685–689. doi:10.1016/S1004-9541(06)60135-3

Coutinho, J.A.P., 1998. Predictive UNIQUAC: A new model for the description of multiphase solid-liquid equilibria in complex hydrocarbon mixtures. Ind. Eng. Chem. Res. 37, 4870–4875. doi:10.1021/ie980340h

Coutinho, J.A.P., Knudsen, K., Andersen, S.I., Stenby, E.H., 1996. A local composition model for paraffinic solid solutions. Chem. Eng. Sci. 51, 3273–3282. doi:10.1016/0009-2509(95)00397-5

Coutinho, J.A.P., Ruffier-Méray, V., 1997. Experimental Measurements and Thermodynamic Modeling of Paraffinic Wax Formation in Undercooled Solutions. Ind.Eng.Chem. Res 36, 4977–4983. doi:10.1021/ie960817u

Coutinho, J.A.P., Stenby, E.H., 1996. Predictive Local Composition Models for Solid / Liquid Equilibrium in n -Alkane Systems : Wilson Equation for Multicomponent Systems. Ind. Eng. Chem. Res. 35, 918–925. doi:10.1021/ie950447u

Dimitriou, C.J., 2013. The rheological complexity of waxy crude oils : Yielding , thixotropy and shear heterogeneities. Massachusetts Institute of Technology, PhD Thesis, USA.

Dimitriou, C.J., McKinley, G.H., Venkatesan, R., 2011. Rheo-PIV analysis of the yielding and flow of model waxy crude oils. Energy & Fuels 25, 3040–3052. doi:10.1021/ef2002348

Ding, J., Zhang, J., Li, H., Zhang, F., Yang, X., 2006. Flow behavior of Daqing waxy crude oil under simulated pipelining conditions. Energy and Fuels 20, 2531–2536. doi:10.1021/ef060153t

Erickson, D.D., Niesen, V.G., Brown, T.S., 1993. Thermodynamic measurement and prediction of paraffin precipitation in crude oil. Proc. - SPE Annu. Tech. Conf. Exhib. Pi, 933–948. doi:10.2523/26548-MS

Ghanaei, E., Esmaeilzadeh, F., Fathikalajahi, J., 2012. Wax formation from paraffinic mixtures: A simplified thermodynamic model based on sensitivity analysis together with a new modified predictive UNIQUAC. Fuel 99, 235–244. doi:10.1016/j.fuel.2012.03.053

Guozhong, Z., Gang, L., 2010. Study on the wax deposition of waxy crude in pipelines and its application. J. Pet. Sci. Eng. 70, 1–9. doi:10.1016/j.petrol.2008.11.003

Hammami, A., Raines, M.A., 1999. Paraffin Deposition From Crude Oils: Comparison of Laboratory Results With Field Data. SPE J. 4, 9–18. doi:10.2118/54021-PA

Hansen, J.H., Fredenslund, A., Pedersen, K.S., Rønningsen, H.P., 1988. A Thermodynamic Model for Predicting Wax Formation in Crude Oils. AIChE J. 34, 1937–1942. doi:10.1002/aic.690341202

Ilyin, S., Arinina, M., Polyakova, M., Bondarenko, G., Konstantinov, I., Kulichikhin, V., Malkin, A., 2016. Asphaltenes in heavy crude oil: Designation, precipitation, solutions, and effects on viscosity. J. Pet. Sci. Eng. 147, 211–217. doi:10.1016/j.petrol.2016.06.020

Imai, T., Nakamura, K., Shibata, M., 2001. Relationship between the hardness of an oil–wax gel and the surface structure of the wax crystals. Colloids Surfaces A Physicochem. Eng. Asp. 194, 233–237. doi:10.1016/S0927-7757(01)00799-3

Jemmett, M.R., Magda, J.J., Deo, M.D., 2013. Heterogeneous Organic Gels: Rheology and Restart. Energy & Fuels 27, 1762–1771. doi:10.1021/ef3014629

Jones, A.G., 2002. Crystallization process systems. Butterworth-Heinemann, London, UK.

Kané, M., Djabourov, M., Volle, J.L., Lechaire, J.P., Frebourg, G., 2003. Morphology of paraffin crystals in waxy crude oils cooled in quiescent conditions and under flow. Fuel 82, 127–135. doi:10.1016/S0016-2361(02)00222-3

Kok, M. V, Létoffé, J.M., Claudy, P., Martin, D., Garcin, M., Vollet, J.L., 1996. Comparison of wax appearance temperatures of crude oils by differential scanning calorimetry, thermomicroscopy and viscometry. Fuel 75, 787–790.

Lopes-da-Silva, J.A., Coutinho, J.A.P., 2007. Analysis of the isothermal structure development in waxy crude oils under quiescent conditions. Energy & Fuels 21, 3612–3617. doi:10.1021/ef700357v

Maqbool, T., Srikiratiwong, P., Fogler, H.S., 2011. Effect of Temperature on the Precipitation Kinetics of Asphaltenes. Energy & Fuels 25, 694–700. doi:10.1021/ef101112r

Marchesini, F.H., Alicke, A.A., de Souza Mendes, P.R., Ziglio, C.M., 2012. Rheological characterization of waxy crude oils: Sample preparation. Energy & Fuels 26, 2566–2577. doi:10.1021/ef201335c

Mendes, R., 2015. Rheological behavior and modeling of waxy crude oils in transient flows. Tese de Doutorado, Université Paris-EST, França.

Mortazavi-Manesh, S., Shaw, J.M., 2014. Thixotropic rheological behavior of maya crude oil. Energy and Fuels 28, 972–979. doi:10.1021/ef4022637

Mullin, J., 2001. Crystallization. 4th ed. Butterworth-Heinemann, London.

Nývlt, J., Hostomsky, J., Giulietti, M., 2001. Cristalização. EdUFSCar/IPT, São Carlos - SP.

Oliveira, G.M., Negrão, C.O.R., 2015. The effect of compressibility on flow start-up of waxy crude oils. J. Nonnewton. Fluid Mech. 220, 137–147. doi:10.1016/j.jnnfm.2014.12.010

Oliveira, M.C.K., Teixeira, A., Vieira, L.C., Carvalho, R.M., Carvalho, A.B.M., Couto, B.C., 2012. Flow assurance study for waxy crude oils. Energy & Fuels 26, 2688–2695. doi:10.1021/ef201407j

Paso, K.G., Krückert, K.K., Oschmann, H.-J., Ali, H., Sjöblom, J., 2014. PPD architecture development via polymer–crystal interaction assessment. J. Pet. Sci. Eng. 115, 38–49. doi:10.1016/j.petrol.2014.02.002

Pedersen, K.S., Skovborg, P., Rønningsen, H.P., 1991. Wax Precipitation from North Sea Crude Oils. 4. Thermodynamic Modeling. Energy & Fuels 924–932.

Pedersen, K.S., Thomassen, P., Fredenslund, A., 1984. Thermodynamics of Petroleum Mixtures Containing Heavy Hydrocarbons. 1. Phase Envelope Calculations by Use of the Soave-Redlich-Kwong Equation of State. Ind. Eng. Chem. Process 23, 163–170. doi:10.1021/i200024a027

Prausnitz, J.M., Lichtenthaler, R.N., Azevedo, E.G., 1986. Molecular Thermodynamic of Fluid-Phase Equilibria, 2nd edn. ed. Prentice-Hall, Englewood Cliffs, USA.

Rønningsen, H.P., Bjorndal, B., Hansen, A.B., Pedersen, W.B., 1991. Wax precipitation from North Sea crude oils. 1. Crystallization and dissolution temperatures, and Newtonian and non-Newtonian flow properties. Energy & Fuels 5, 895–908. doi:10.1021/ef00030a019

Santos, J.S.T., 2009. Experimental and numerical study of paraffination in hydrocarbon flow in pipelines producer. PhD Thesis, COPPE/UFRJ, Brazil (in portuguese).

Sloan, E.D., Koh, C.A., 2008. Clathrate Hydrate of Natural Gases. 3rd ed. Taylor & Francis Group, Boca Raton, FL, Estados Unidos.

Stefanescu, D.M., 1988. ASM Metals Handbook - Casting. 9th ed. ASM International, Estados Unidos.

Taggart, A.M., Voogt, F., Clydesdale, G., Roberts, K.J., 1996. An Examination of the Nucleation Kinetics of n-Alkanes in the Homologous Series C13H28 to C32H66 , and Their Relationship to Structural Type, Associated with Crystallization from Stagnant Melts. Langmuir 12, 5722–5728. doi:10.1021/la9600816

Tarcha, B. a., P. Forte, B.P., Soares, E.J., Thompson, R.L., 2015. Critical quantities on the yielding process of waxy crude oils. Rheol. Acta 479–499. doi:10.1007/s00397-015-0835-1

Venkatesan, R., Nagarajan, N.R., Paso, K., Yi, Y.B., Sastry, A.M., Fogler, H.S., 2005. The strength of paraffin gels formed under static and flow conditions. Chem. Eng. Sci. 60, 3587–3598. doi:10.1016/j.ces.2005.02.045

Venkatesan, R., Östlund, J.A., Chawla, H., Wattana, P., Nydén, M., Fogler, H.S., 2003. The effect of Asphaltenes on the Gelation of Waxy Oils. Energy & Fuels 17, 1630–1640. doi:10.1021/ef034013k

Vieira, L.C., 2008. The influence of pressure on the crystallization of crude oils paraffin. PhD Thesis, IMA/UFRJ, Brazil (in portuguese).

Wardhaugh, L.T., Boger, D.V., 1987. Measurement of the unique flow properties of waxy crude oils. Chem. Eng. Res. Des. 65, 74–83.

Webber, R.M., 1999. Low temperature rheology of lubricating mineral oils: Effects of cooling rate and wax crystallization on flow properties of base oils. J. Rheol. 43, 911–931. doi:10.1122/1.551045

Won, K.W., 1989. Thermodynamic calculation of cloud point temperatures and wax phase compositions of refined hydrocarbon mixtures. Fluid Phase Equilib. 53, 377–396.

Won, K.W., 1986. Wax Phase Formation. Fluid Phase Equilib. 30, 265–279.

Zhao, Y., Paso, K., Sjöblom, J., 2014. Thermal behavior and solid fraction dependent gel strength model of waxy oils. J. Therm. Anal. Calorim. 117, 403–411. doi:10.1007/s10973-014-3660-3

Zhou, X., Thomas, F.B., Moore, R.G., 1996. Modelling of Solid Precipitation from Reservoir Fluid. J. Can. Pet. Technol. 35, 35–45.

Zílio, E.L., Pinto, U.B., 2002. Identification and distribution of the main groups of components present in brazilian crude oils. Bol. Técnico da Petrobras 45, 21–25.

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