



## Full Length Article

# The importance of supersaturation on determining the solid-liquid equilibrium temperature of waxy oils



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## HIGHLIGHTS

- A supercooling is required for the onset of wax precipitation in waxy oils.
- The higher the cooling rate the higher the metastable region width.
- The cooling experiment is not appropriate to determine the saturation temperature.
- At a high heating rate, there also exists a superheating during the dissolution.
- The saturation temperature can be determined at a very low heating rate.

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## ABSTRACT

Crystallization is a process where an ordered solid structure is formed from a disordered phase. This event is divided in two main stages, namely nucleation and crystals growth. As paraffin nucleation is a stochastic process, a supercooling is needed to initiate the process. In other words, the beginning of crystal precipitation does not coincide with the highest thermodynamic solid-liquid equilibrium temperature. Therefore, during the cooling it is required that the fluid reaches a certain temperature below saturation, i.e., a metastable state, to initiate the crystal nucleation process. The difference between the saturation temperature and the crystallization temperature is called degree of supercooling. As this metastable condition may exist during not only the crystallization but also the dissolution of crystals, this work proposes a procedure to determine consistently the highest solid-liquid thermodynamic equilibrium temperature by using the results of rheometer and DSC experiments. It can be anticipated that the proposed protocol states that the highest solid-liquid thermodynamic equilibrium temperature is considered to approach the dissolution temperature when the material is heated at a very low heating rate.

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## 1. Introduction

Crude oil is a complex mixture of hydrocarbons, heteroatoms (e.g. N, S, O) and inorganic components as salts, sand and water [1,2]. More than 90% of the oil can be composed of hydrocarbons [3] that are usually divided in four major fractions: saturates – known as paraffin, aromatics, resins and asphaltenes (SARA) [4–6]. At oil reservoir conditions, i.e. high temperatures

(70–150 °C) and pressures (50–100 MPa), all the paraffin molecules are dissolved in the oil so that this mixture of hydrocarbons is in liquid phase [7] and behaves as a Newtonian fluid [8]. At low temperatures, the solubility of high molecular weight components in the oil decreases and mainly the n-paraffins tend to precipitate out of the solution as crystal structures. These crystals that render a non-Newtonian behavior to the fluid [9,10], with a variety of characteristics such as pseudo-plasticity, elasticity, time-dependency [11,12] and/or deformation dependency [13], may deposit in the inner surface of pipelines [14,15] and are responsible for oil gelation when the flow is interrupted [5,16]. The risk of wax crystal precipitation during offshore production is quite high, as the ocean floor temperature could be as low as 4 °C [17].

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The wax deposition in pipeline inner surfaces increases pump power, decreases flow rate and, consequently, reduces oil production [14,18]. The common methods employed to remediate wax deposition (e.g. the use of chemical inhibitors, pipeline heating and mechanical removal by using pigs) are extremely costly in deep and ultra-deep water production scenarios [17]. In flow interruption for pipeline maintenance, gelation takes place and start-up pressures much larger than the usual operational pressure are required to break down the gel structure [19,20]. If the rheological properties of waxy crude oils at low temperatures are not accurately determined, restart pressures can be overrated leading to overestimation of pipe dimensions, and consequently making pipeline projects unfeasible [21,22].

A key point in crude oil production and transportation is the wax crystallization onset temperature. The accurate determination of this temperature is important to design production and/or transportation pipelines to work above this temperature and to know when the crystallization becomes a real problem in oil production. This temperature, however, may be distinct from the highest temperature in which the solid and liquid phases co-exist in equilibrium at a fixed pressure. The latter is a thermodynamic property and is known as the highest solid-liquid thermodynamic equilibrium temperature,  $T_{eq,SL}$ . In petroleum area, this temperature is usually called the Wax Appearance Temperature (WAT) or cloud point [1]. Although there is not a consensus in the open literature, Tiwary and Mehrotra [23] claimed that “WAT is the true solid-liquid phase boundary temperature”.

Researchers have made significant effort to model the thermodynamic solid-liquid equilibrium [24–39]. The general solid-liquid equilibrium is reached when the fugacities of each component “*i*” in the solution are identical in solid and liquid phases. Many assumptions have been made to determine the solid-liquid equilibrium of waxy oils by means of thermodynamic models. Some authors assume that the difference between the heat capacities of each component is negligible ( $\Delta C_{p,i}^{SL} = 0$ ) [25,28,31] and the decrease in component volume due to phase transition is disregarded in some cases [27]. The liquid phase is assumed to be an ideal solution ( $\gamma_i^L = 1$ ) by some authors [34,40] and some others consider that  $\gamma_i^S = 1$  [36,40], where  $\gamma_i$  is the activity coefficient of each component present in the solution. The regular solution is used in many works [25–28,33,40] to take the non-idealities of the liquid and solid phases into account. In addition to these assumptions, the liquid phase activity coefficient was also determined by Flory-Huggins model [36], by Flory free-volume equation added to a UNIFAC residual term [41] and by Flory free-volume model [35]. The solid phase non-ideality was also considered by Wilson equation [40,41] and by UNIQUAC model [32,34,35,37,39,40]. Although some models performed better than others in many comparisons, there is not a capable model to predict the solid-liquid equilibrium temperature of all waxy oils. The differences between experimental and calculated  $T_{eq,SL}$  are generally higher than 2 °C for the cases in which  $T_{eq,SL}$  is approximately 20 °C and the crystals mass fraction below the equilibrium temperature is not accurately determined but only qualitatively well represented.

On the other hand, the experimental methods to find the highest solid-liquid equilibrium temperature of waxy oil are not well consolidated. Several techniques have been used to determine the WAT: Visual Method [23,42,43] as normalized by ASTM [44], Filter Plugging (FP) [45,46], Viscometry [46–51], Densitometry [52], Cross Polar Microscopy (CPM) [23,47,48], Differential Scanning Calorimetry (DSC) [5,12,53–60], cold finger [45], ultrasonic experiments [61], Fourier Transform Infrared (FTIR) energy scattering technique [45] and Near Infrared (NIR) scattering technique [62]. Rønningsen et al. [47] analyzed 17 crude oils by comparing

the three more usual methods – microscopy, differential scanning calorimetry and viscometry – and concluded that microscopy is the best method to determine the WAT. In contrast, Kok et al. [48] used the same three techniques to investigate 15 different crude oils and claimed that the best method to determine the wax appearance temperature depends on the solution composition. Tiwary and Mehrotra [23] examined different model waxy oils using the same three techniques again and compared with a visual method. The authors concluded that the DSC was the best technique to determine the solid-liquid equilibrium temperature because provided the highest WAT values. Different techniques proposed to determine more accurately the WAT [45,52,62] have been compared with the usual techniques and some interesting conclusions were obtained. Although Marchesini et al. [9] have made a wise discussion saying that the temperature determined by viscometry/rheometry is not the solid-liquid equilibrium temperature because the first crystal that appears in the solution is too small to change the oil viscosity (the same can be concluded from the other techniques [23]), a key point in wax crystallization, i.e., the supercooling has been forgotten or neglected by the majority of the authors. It is worth mentioning that just few authors [17,31,43,63] recognized the existence of this metastable region before the wax crystallization.

Crystallization is a process of building up an ordered solid structure from a disordered phase and involves two main stages: nucleation and crystal growth [47,64]. As well known and consolidated in the inorganic chemistry area, nucleation is a stochastic process that requires a supercooling (or supersaturation) to start it up [65–67]. In other words, crystals precipitation begins at a temperature that is below the solid-liquid equilibrium temperature, which is a thermodynamic property [37]. In the current work, the highest solid-liquid equilibrium temperature is represented by  $T_{eq,SL}$  and the onset of wax precipitation is defined by the crystallization temperature,  $T_c$ , as proposed by Marchesini et al. [9]. To avoid confusion with the solid-liquid equilibrium state, the term WAT (Wax Appearance Temperature) is not used here. The difference between the solid-liquid equilibrium temperature and the crystallization temperature is defined as degree of supercooling,  $\Delta T_{sup}$ , [65,66]:

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

Considering that during heating solid may also exist in a non-equilibrium condition in the solution [60,68] and consequently metastable states may occur in either crystallization or dissolution of crystals, this work presents a discussion about how to evaluate consistently the highest solid-liquid equilibrium temperature of waxy oil. The discussion is based on the results of rheometer and  $\mu$ DSC 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 section

The experiments presented in the current work were conducted with model waxy oils. The model oils were formulated by adding a paraffin wax with a melting point between 58 and 62 °C (Sigma Aldrich 327212 CAS-No:8002-74-2) to a mineral oil (Sigma Aldrich 330779 – CAS-No: 8042-47-5). The paraffin wax and mineral oil were the same used in Dimitriou’s thesis [69], by others in his group [70] and by *IFP Energies nouvelles’s work* [71]. The wax is composed of 60 wt% n-paraffins and 40 wt% iso and cycloparaffins [70]. The normal alkane carbon distribution of both

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