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ON THE INFLUENCE OF MICRO- AND MACRO-CRISTALLINE PARAFFINS ON THE PHYSICAL AND RHEOLOGICAL PROPERTIES OF CRUDE OIL AND ORGANIC SOLVENTS

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Abstract. The influence of micro- and macro-crystalline paraffins on the properties of crude oil and organic solvents was investigated. Micro-cristalline paraffins promote the most pronounced changes in the investigated physical and rheological properties of all tested solutions. The concentration of branched-alkanes in paraffins is the pivotal parameter that promotes these changes.

Keywords: flow of waxy crude, micro- and macro-paraffins, rheological properties, wax appearance temperature, yield stress.

1. Introduction

Waxy crude oil is a complex mixture that may contain up to thousands of different molecules, encompassing a broad range of sizes and shapes ranging from relatively simple gaseous, liquid and solid alkanes to large-size molecules such as resins and asphaltenes. This complex molecular composition poses a challenge to get a better understanding of the physical and rheological properties of crude oil and to anticipate phase equilibria transitions, such as wax appearance temperature (WAT), pour point, and gelation.

In general, waxy crude oil predominantly contains in its composition *n*-paraffins and minor amounts of branched and cyclic paraffins. However, a few waxy crude oils contain *n*-paraffins in small proportion in relation to the branched and cyclic ones, thence showing a strong predisposition to gelation at low temperatures. According to J. Hunt [1] authigenic biodegration processes that take place during the geological time might reduce dramatically the n-paraffins concentration in crude oil. Microorganisms feed preferentially from light *n*-alkanes. Therefore, biodegraded crude oil lacks the intermediate to heavy n-alkanes fraction.

It is well known that waxy crude oils during the production process can go through liquid-solid phase transition at temperatures below the WAT. This transition phenomenon is believed to be controlled by the so-called "*weak van der Waals forces*" that develop between different tiny wax crystallites at low temperatures [2]. G. Holder and J. Winkler [3] invoke the "*...overlapping and interlocking of the needle-shaped paraffin crystals...*" as the primary mechanism of waxy crude oil's gelation. H. Ronningsen [4], for his part, recalls an earlier model in which the gelled crude oil is compared to polymer gels, and it is yielding behavior being linked to the "*...rupture of bond linkages within the crystal network...*". According to R. Visintin *et al.* [5] there is a body of data that supports that this gelation process results from the creation of "*... a network of wax crystals that present a strong affinity...*". Furthermore, "*...the fast flocculation of wax crystallites, as soon as they have been formed in solution...*", is also invoked by E. Vignatti *et al.* [6] to explain this gelation process. Despite the research efforts on this matter, waxy crudes gelation mechanisms remain contentious in many aspects.

In fact, a consensus does not exist on how the multi-faceted phase transition processes do develop. Another point worth noting is that under actual field conditions waxy crude oils may be also commingled with different solid and liquid materials such as: organic solids (paraffins, asphaltenes, naphthenates); inorganic solids (scales, rock clasts, and pipe rust); hydrate crystals, and; emulsified – water. According to C. Bai and J. Zhang [7] the concentration of dispersed wax aggregates in crude oils "*… may vary by orders of magnitude, thence*

promoting dramatic changes in their rheological and/or flowing characteristics, chiefly in low temperature flowing conditions…" In whatever way these aggregates promote these changes is a dimly understood matter [8, 9]. Again, considerable disagreements still remain on the physical and chemical variables that are most influential in both characteristics [10].

The recent discoveries of large reserves of waxy crude oils in Brazilian coastal waters were the impetus to carry out a study to bracket the effect of different waxes on the physical and rheological properties of these waxy crude oils. It is important to emphasize that the following conditions are recurrent in those coastal waters scenarios: low subsea temperatures, well completion schemes that include long tie-backs, subsea manifolds and X-trees, downhole chemicals injection systems, and well architecture for high flowrate production. Briefly, these conditions are prone to create scenarios for the precipitation, deposition and gelling of paraffins indigenous to these crudes. Should these much unanswered questions be solved, it could help avoiding production loss problems, and reducing additional CAPEX (capital expenditure) required to build a production facility with oversized-and/or redundant-operational capabilities [11].

The aim of this technical contribution is to shed some light upon these flow assurance (FA) puzzles. To accomplish that, an experimental study was carried out to gauge the effects of micro- and macro-crystalline paraffins on the properties of crude oil, and some other solvents as well. Samples of lab standard micro- ("Mic-wax") and macro ("Mac-wax")-crystalline paraffins were characterized and accurately blended to the following solvents: kerosene, n-paraffin blend (C_{13}–C_{15} cut), dodecane, DTC blend (a mixture of equal parts of decane, toluene and cyclohexane); and crude oil. Concise laboratory experiments were carried out to bracket the effect of both types of paraffin on the yield stress, pour point, and WAT of the prepared solutions. The role of organic solvents on the paraffins aggregation process was investigated as well. The results of this ongoing research study show that – in relation to Mac-wax – Mic-wax promotes a more pronounced effect on the investigated physical and rheological properties of the tested solutions.

2. Experimental

2.1. Materials and Methods

The analytical grade paraffin samples used in this experimental study were supplied by Fluka Analytical Reagents Brazil, as follows: i) – microcrystalline paraffin (catalog product # 76232), and; ii) – macrocrystalline paraffin (catalog product # 76228). These samples were analytically characterized in our laboratories and used "as is" in this study, without going through any further

purification processes. In this work these samples were named: "Mic-wax" and "Mac-wax", respectively. Some physical and chemical properties of these samples are depicted in Table 1 and their carbon number distribution is depicted in Fig. 1. From Fig. 1 it is possible to distinguish the carbon number distribution of Mic-wax from Mac-wax. On the one hand, Mac-wax shows the highest percentage of C_{24} and C_{25} straight chain (normal) alkanes (*circa* 90.0 %). In fact, the melting point of Mac-wax is controlled by the normal alkanes chain length. On the other hand, the normal-alkanes fraction in Mic-wax is somewhat lower (*circa* 64.5 %), the mean normal alkane chain length is C_{37}, and the branched *iso*-alkanes predominantly contain chain lengths up to C_{39}. Mic-wax also contains a relatively high percentage of branched (*iso*) and cyclic (naphthenic) – alkanes. Heavy normal alkanes (C_{40}+) are also present, in small amount, in the Mic-wax composition. At last, mic-wax is denser, more viscous, elastic and flexible than Mac-wax.

2.2. Mic- and Mac-wax Solutions and Supporting Analytical Apparatuses

A series of wax laden (5 and 10 % w/w concentration) solutions and/or dispersions (thenceforward named fluid systems) was prepared with both Mic- and Mac-wax samples. The following solvents were used: n-paraffins (cut of C_{13}-C_{15}) blend (supplied by Petrobras RLAM Refinery, Bahia state, Brazil), analytical grade dodecane (purchased from Merck Analytical Chemicals), DTC, kerosene (QAV-type kerosene supplied by Petrobras REDUC Refinery, Rio de Janeiro state, Brazil), and crude oil (from an offshore field located in the Southeastern Brazilian coast). These fluid systems were prepared at ambient temperature (*circa* 295 K) under a vigorous stirring provided by a magnetic stirrer (IKA model RCT). After that, they were transferred to a closed vessel and heated up to 353 K during 1 h. Following that, the fluid systems were submitted to a suite of physical and chemical assays significant to FA related issues. Some characteristics of the solvents used to dilute and/or disperse both wax samples are depicted in Table 2.

It is out of scope of the present work to provide a detailed description of the analytical apparatuses and/or tools used in this study. However, a brief description of them and their specific applications follows: the wax appearance temperature (WAT) of the samples was determined by differential Scanning Micro-Calorimety (Setaram, model μ-DSC-VII); the pour point of the samples was determined according to ASTM D-97 standard method [12]; a Haake model Mars III rheometer operating on a parallel plate geometry mode was used to carry out the rheological study of the fluid systems, and; clear field and cross-polarized microphotographs of particular fluid systems were taken under a Carl Zeiss microscope (Axiomatic model).

Physical and chemical properties of Mic- and Mac-waxes used in the study

Investigated parameter	Mic-wax	Mac-wax
Solidification temperature, K	341–347	317–319
n-Paraffin, wt %	64.5	90.0
iso-Paraffin, wt %	35.5	10.0
Average molecular weight, amu	659.95	477.42

a)   b)
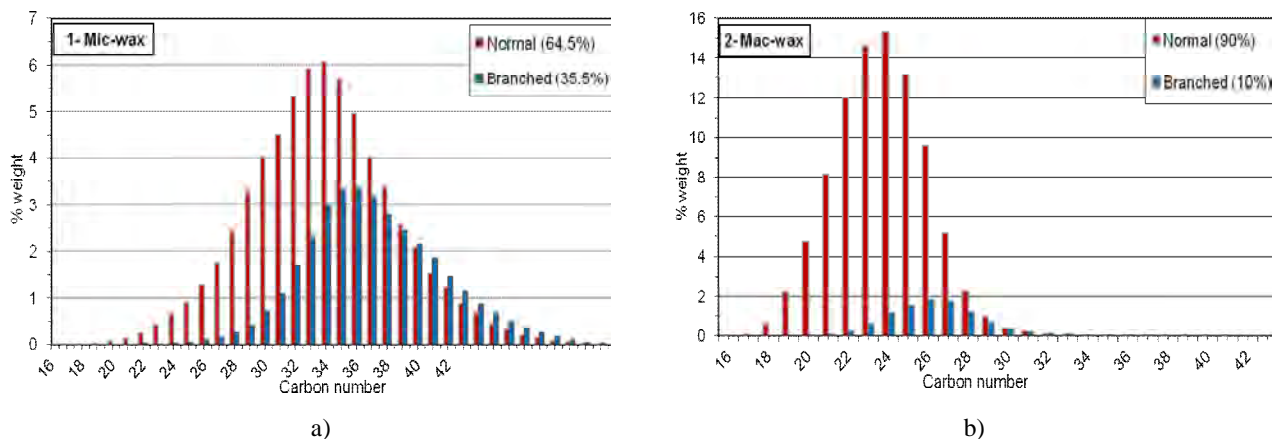
Fig. 1. Carbon number distribution of lab-standard samples: Mic-wax (a) and Mac-wax (b)

Some characteristics of the solvents used to prepare Mic- and Mac-wax fluid systems

Solvents	*n*-Paraffins blend	Dodecane	DTC blend	Kerosene	Crude oil
Pour point, K	264.0	ND	ND	ND	12.0
WAT, K	274.7	258.3	< 253.0	< 253.0	312.5

Note: ND – not determined but lower than 273 K.

2.3. Pour Point (PP) Determination

The PP of the fluid systems prepared for this study was determined according to the ASTM D-97 standard method.

2.4. Rheological Measurements for Yield Stress Determination

A suite of experiments was carried out to measure the yield stress of the fluid systems, as follows: pre-heating the sample at 353 K in a closed vessel; running the oscillatory rheological experiments; cooling down (1 K·min^{-1} rate) the sample up to 277 K; and allowing the sample to rest under static conditions for 15 min to mimic the gelation process that takes place during production shutdowns. Triplicate fresh samples were used in each run. The results were analyzed with the aid of software provided by the rheometer manufacturer. Oscillatory experiments were performed at 1 Hz frequency, thence submitting the fluid system samples to stresses ranging from 10^{-2} to 10^{3} Pa, as a means to examine the internal structure of the gelled wax-in-solvent samples. The storage modulus (G') and loss modulus (G''), expressed in Pa, stand for the elastic and viscous characteristics of the fluid sample, respectively [13]. The yield stress, for its part, is determined by the intersection point of the curves of loss- and storage-moduli = 277 K (Fig. 2).
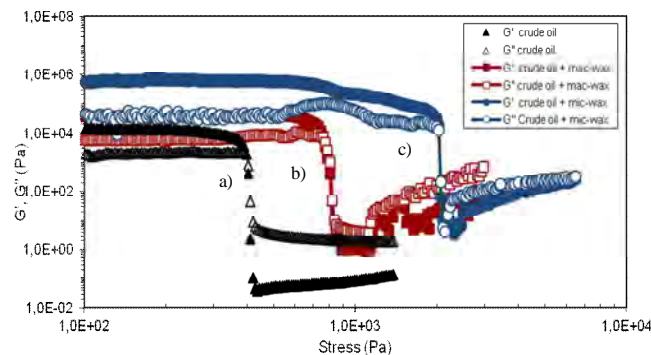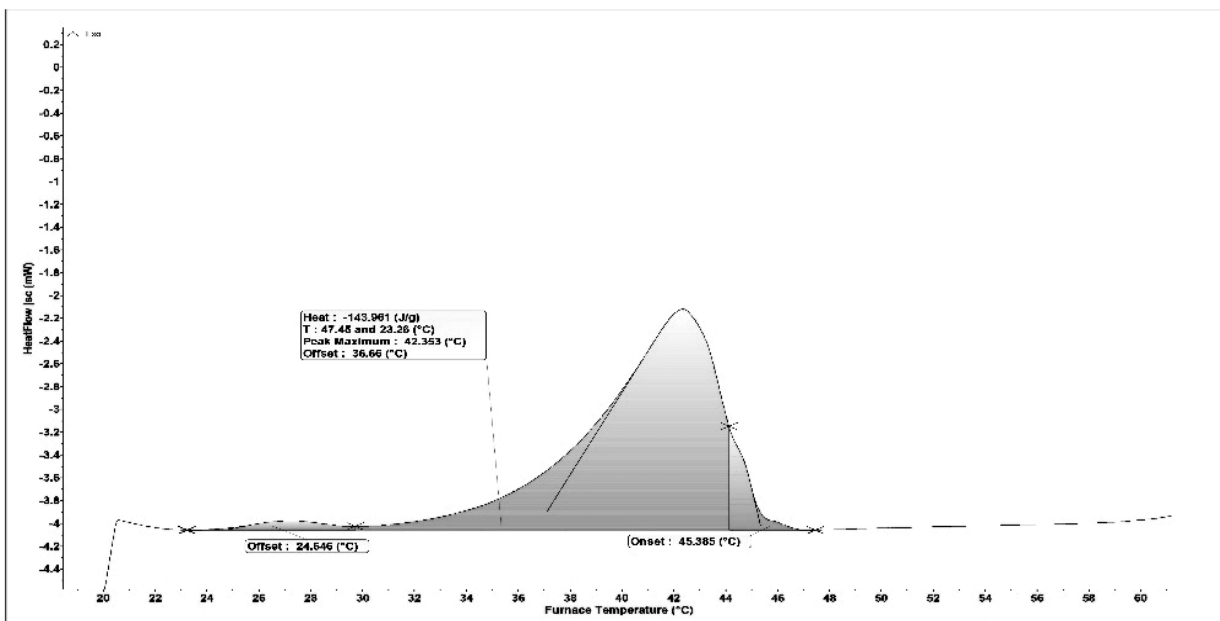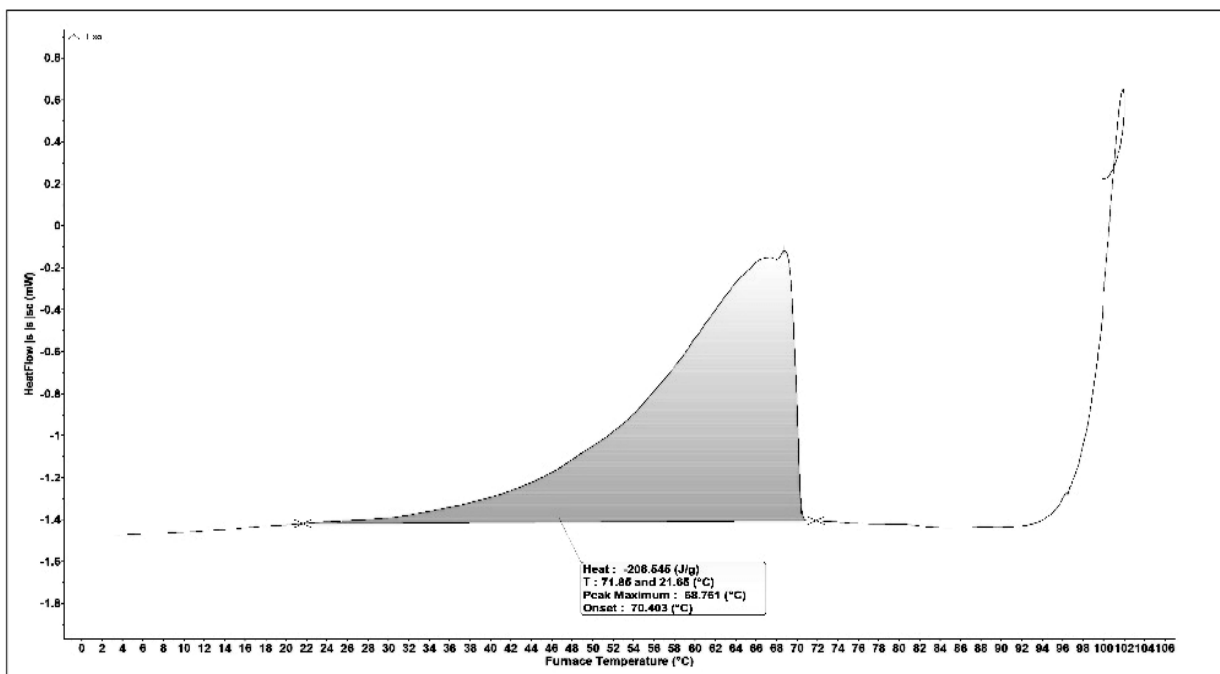

Fig. 2. Yield stress measurement for: pure crude oil (a); crude oil + 5 % Mac-wax (b) and crude oil + 5 % Mic-wax (c) samples (tests performed at 277 K)

a)

b)

Fig. 3. μ-DSC thermograms of Mic-wax (a) and Mac-wax (b)

2.5. Wax Appearance Temperature Determination

The µ-DSC analytical apparatus, which has been referred to in Subsection 2.2, was used to determine the WAT of the fluid systems prepared for this study. According to an in-house developed analytical procedure, the thermal memory of all fluid systems under investigation was previously eliminated by pre-heating the DSC sample containing crucible $\cong$ 353 K (1 h time lapse). Statistical evidences show this procedure helps increasing the repeatability of WAT results [14, 15]. Following this heating stage, both the sample containing and the reference (hollow) crucibles of the µ-DSC apparatus are submitted to a controlled cooling process. Namely, the samples were slowly cooled from 353 down to 273 K at a controlled cooling rate (0.8 K·min^{-1}). It is important to emphasize that our experience with this analytical technique shows that the use of low cooling rates optimizes the detection of the onset of paraffins crystallizationin crude oil and minimizes the subcooling of the samples as well.

The following Fig. 3 depict the typical micro-thermogram spectra (temperature *vs.* heat flow plots)

obtained from Mic-wax and Mac-wax – laden fluid systems (Fig. 3a and 3b, respectively). The total exothermic heat flow associated with the wax crystallization phenomenon (enthalpy of crystallization, $\Delta H_{crystallization}$) can be obtained by computing the integral of the blue-shaded area enclosed by the cooling temperature curve and the base line [16]. By the same token, the WAT can be automatically determined by µ-DSC: it is the onset temperature at which the cooling rate curve, $\Delta T \cdot \Delta t^{-1}$, starts changing its slope and detaches from the baseline.

2.6. Microphotographs of Selected Fluid Systems

A series of microphotographs was also taken to identify the morphology of Mic-wax- and Mac-wax-laden fluid systems. Both Figs. 4 and 5 show the crystalline network that both Mic- and Mac-wax are able to form in mineral oil. The microscope visualization techniques (cross-polarized light and clear field) that have enabled to produce these outstanding microphotographs are being developed with cooperation of the School of Chemistry of Rio de Janeiro Federal University at Rio de Janeiro.
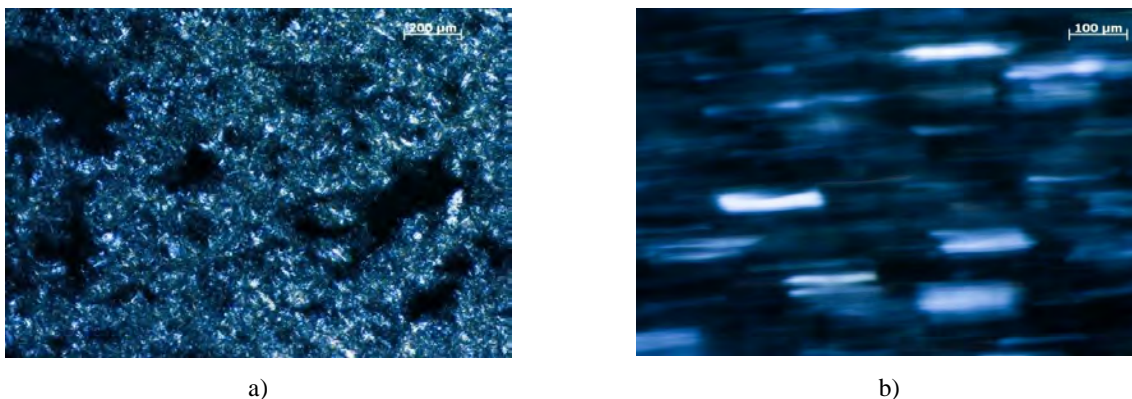

a)   b)

Fig. 4. Cross-polarized light microphotographs (cover glass slides placed over sample, magnification of 10x) at 295 K: 5 % Mic-wax in mineral oil (a) and 5 % Mac-wax in mineral oil (b)
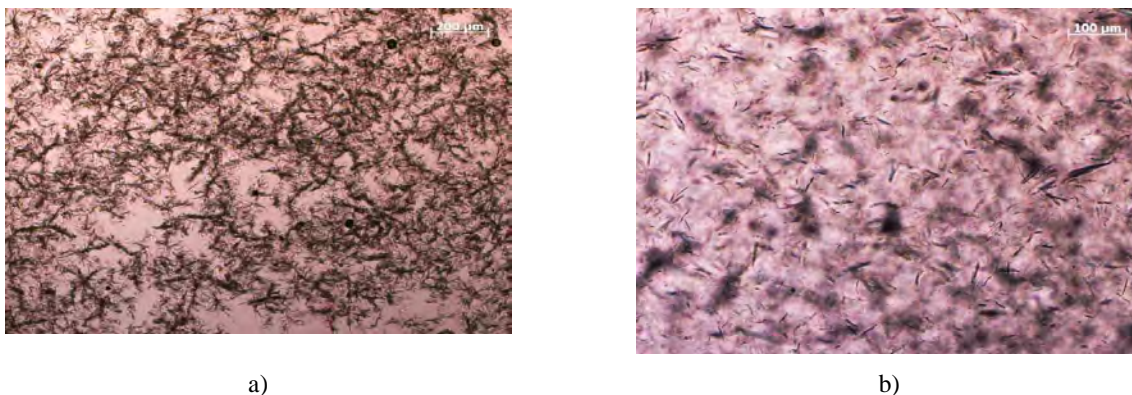

a)   b)

Fig. 5. Clear field microphotographs at 295 K: 5 % Mic-wax in mineral oil (a) (cover glass slides placed over sample, magnification of 10x) and 5 % Mac-wax in mineral oil (b) (droplet over glass slide, magnification of 10x)

2.7. Photographs of Solutions of Mic- and Mac-wax in Santos Basin Crude Oil

Fig. 6 depicts two photographs of crude oil samples containing 5 wt % of Mic- and Mac-wax, respectively. These glass flasks were photographed upside down to emphasize the dissimilar rheological behavior of the samples ($\cong$ 293 K). Notice that the left side sample – the one containing Mic-wax – does not flow under ambient gravitational field.

Fig. 6. The effect of Mic- (at the left) and Mac-wax (at the right) on the flowing properties of crude oil used in the study

3. Results and Discussion

A compilation of the main experimental results of this study is presented in Table 3.

Glancing over Table 3 it is possible to distinguish the pronounced effect of Mic-wax on: pour point, WAT, crystallization enthalpy, yield stress, and turbidity of the different fluid systems used in the study. In addition, the most pronounced effect of both paraffins on the investigated properties was obtained when n-paraffin was used as the solvent of the fluid system. All else being equal, solutes and solvents with similar molecules interact in the strongest manner. These findings are consistent with the theory of macromolecules in solutions [17].

A bar chart graph (Fig. 7) compiled from data presented in Table 3 was built to help compare the physical and chemical properties of all fluid systems under investigation.

A collection of discussions on the results of this experimental study is presented as follows:

The resilient elastic characteristics presented by Mic-wax is caused by the massive presence of non-straight (branched and cyclic) paraffins. In fact, Mic-wax crystals are small and thin, thence being more flexible than Mac-wax ones. Furthermore, the branched structures allow solvent or crude oil molecules to be more efficiently entrapped in the crystal lattice. Further studies on this matter, however, are necessary to corroborate this hypothesis.

Should a Mic-wax-containing crude oil be cooled down below the PP, a relatively higher pressure is required to resume its flow and/or restart the production. It is interesting to mention that there is a series of lab and field evidences that some crude oils can flow at temperatures below the pour point without presenting any blockage problems due to gelation, provided they are kept flowing under high shear stress conditions [13]. In reality, the concert of shear forces that act on crude oil flow in pipelines cannot be perfectly mimicked by the ASTM D-97 pour point test performed in the lab with dead oil samples.

Suitable analytical methods to quantify the *n*-alkanes to non-straight alkanes ratio in crude oil have not been developed yet. Traditional analytical tools such as the gas chromatography – mass spectrometry combo conceived to separate and determine different molecular structures do not produce high-resolution data when raw crude oil samples are assayed. On top of that, little is known regarding an analytical methodology that can accomplish with that task.

Table 3

Physical and chemical properties of the fluid systems prepared with Mic- and Mac-wax

| Sample #	Mic-wax, %	Mac-wax, %	Solvent	Pour point, K	Average WAT, K	ΔH at 277 K, J g^{-1}	Yield stress, Pa	Fluid System Turbidity	
								295 K	353 K
1	10	–	*n*-paraffin	294	323.34	205.0	242.9	cloudy	clear
2	–	10	*n*-paraffin	288	287.42	9.4	101.8	clear	clear
3	10	–	dodecane	285	314.25	18.0	110.6	cloudy	clear
4	–	10	dodecane	285	285.78	8.5	0	clear	clear
5	10	–	DTC	285	308.63	17.7	94.9	cloudy	clear
6	–	10	DTC	282	279.85	3.1	2.1	clear	clear
7	10	–	kerosene	288	311.55	17.9	40.7	cloudy	clear
8	–	10	kerosene	282	283.85	7.1	2.8	clear	clear
9	–	–	crude oil	285	312.53	4.9	375.7	opaque	opaque
10	5	–	crude oil	318	318.50	23.33	2373.0	opaque	opaque
11	–	5	crude oil	297	314.55	19.64	1308.0	opaque	opaque
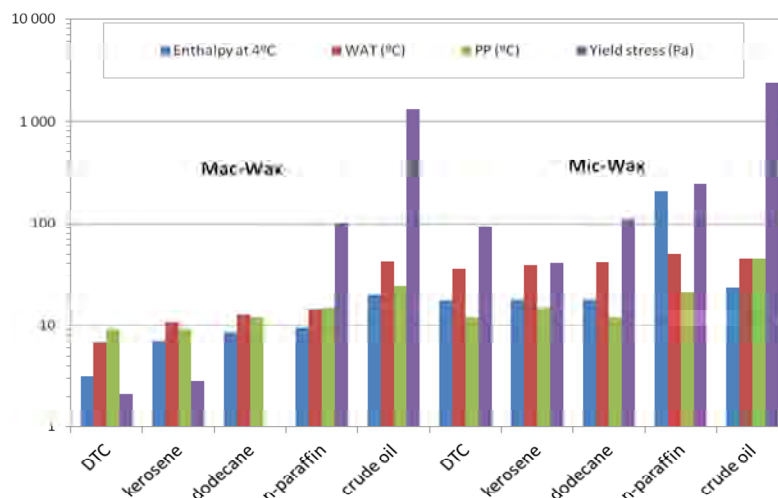
Fig. 7. Physical and rheological properties of the fluid systems used
in this experimental study as a function of the type of paraffin blended with them
(compiled from Table 3)

The optical investigation of the Mic- and Mac-wax fluid systems performed with both clear field and cross-polarized light microscopy has provided evidences on the different paraffin crystal growth patterns developed by each specific wax. Put another way, such a result suggests a more comprehensive use of both optical techniques to investigate the mechanisms of paraffin inhibitors and/or crystal modifiers.

The most pronounced effect of both paraffins on the investigated properties was obtained when n-paraffin was used as the solvent of the fluid system. In fact, solute and solvent interact stronger when they have similar chemical nature [18].

4. Conclusions

Amidst the conclusions that can be drawn from this study are:

In relation to Mac-wax, Mic-wax creates a more pronounced effect on all the physical and rheological properties of the fluid systems that have been investigated in this study. In fact, Mic-wax is prone to form stiff gels; the higher the Mic-wax concentration in the fluid system the stiffer its gel.

The WAT of Mic-wax fluid systems is 4 to 6 times higher than the one presented by the equivalent fluid systems which Mac-wax has been added to. This effect was less pronounced, however, in the fluid systems prepared with crude oil.

Mic-wax can be dissolved or dispersed in all solvents used in the experimental work and display a sharp transition of gel-strength.

The size and morphology of paraffin crystals of Mic- and Mac-wax fluid systems can be determined by clear-field

and cross-polarized light microscopy. The findings of this preliminary study are encouraging to use both optical techniques to investigate the effect of crystal modifiers or crystallization inhibitors on paraffin crystal growth.

Laboratory results show how paraffins can strongly interact with crude oil and change its rheological and flowing properties. This phenomenon, however, strongly depends on crude oil composition. Therefore, as a prescriptive guideline, a case-by-case study must be performed to address these questions. In other words, the findings from a given study cannot be straightforwardly extrapolated to other scenarios.

There is real value in running rheological studies to bracket the influence of these paraffin aggregates on crude oil rheological and flowing properties. These studies, of course, have to be performed prior to the front end engineering design (FEED) process.

Acknowledgements

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ПРО ВПЛИВ МІКРО- І МАКРОКРИСТАЛІЧНИХ ПАРАФІНІВ НА ФІЗИЧНІ ТА РЕОЛОГІЧНІ ВЛАСТИВОСТІ СИРОЇ НАФТИ І ОРГАНІЧНИХ РОЗЧИННИКІВ

Анотація. Досліджено вплив мікро- і макрокристалічних парафінів на властивості сирої нафти і органічних розчинників. Показано, що мікрокристалічні парафіни мають найбільший вплив на фізичні та реологічні властивості досліджуваних компонентів. Встановлено, що концентрація розгалужених алканів в парафінах є ключовим параметром, який зумовлює зміни властивостей.

Ключові слова: парафіниста нафта, мікро- і макропарафіни, реологічні властивості, температура появлення парафіну, межа текучості.