

Wax precipitation in multicomponent hydrocarbon system

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Abstract The objective of this research is to estimate individual effect of various external parameters such as pressure, cooling rate, watercut and addition of mechanical impurities on change in wax appearance temperature (WAT) in oil. In this paper, complex multicomponent system like oil is replaced to simplified model solution, presented by wax in kerosene solution. Research methods in the study were visual method at high-pressure/high-temperature conditions and rheological method under ambient pressure. Experimental results shown that WAT grows with increase in concentration of wax in solution, increase in pressure, watercut, shear rate, addition of mechanical impurities and decrease in gap size of the measuring system (for rheological method). Numerical dependences of WAT in solution on the listed factors are received. Research data are explained by the thermodynamic processes proceeding in model solution. Influence of wax inhibitors addition on process of the crystal structure formation in model solutions and effective wax inhibitors is defined.

Keywords Oil-dispersed system · Precipitation · Aggregates · Wax · Organic deposits

Introduction

WAT is one of key parameters to consider when elaborating protective measures against formation of asphaltene-resin-paraffin deposits in oil wells. WAT is temperature at which the first wax crystal appears in oil (Berne-Allen and Work 1938). Oil is the complex multicomponent dispersion system, and the slightest change in its composition during oil production will significantly impact the change in WAT and the system properties in the whole. Information about individual effect of external parameters on change in WAT in oil will allow to estimate more precisely time and potential wax formation area in the tubing, to diminish the waxing process of oil wells in time and to increase the work over interval of oil wells by application of the most suitable technologies.

Measurement and prediction of wax solubility in oil and model hydrocarbon solutions were carried out by Gudmundsson and Bott (1977), Al-Ahmad et al. (1990), Srivastava et al. (1997) and Wu et al. (2002). Those studies covered the wide range of wax crystallization conditions at various wax concentration.

Measurement of WAT in oil can be carried out by many research methods such as low-resolution pulsed nuclear magnetic resonance (NMR), light-scattering method, ultrasonic method and Fourier-transform infrared spectroscopy (Pedersen et al. 1991; Kok et al. 1996; Elsharkawy et al. 2000; Karan et al. 2000; Jiang et al. 2001; Paso et al. 2009; Jiang et al. 2014; Chen et al. 2014; Huang et al. 2016). However, only few methods are capable to determine the entrapped crude oil in the solid residue correctly. The most effective methods in this context are differential scanning calorimetry (DSC) and proton nuclear magnetic resonance (¹H NMR) (Coto et al. 2011). These techniques allow to estimate the wax precipitation characteristics and

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could be used to further optimize thermodynamic models of wax deposition.

Unfortunately, many of existing methods are expensive, difficult in use and interpretation of the obtained data and require prolonged duration of the experiment, whereas, visual and rheological methods provide simple and rapid measurement of WAT in oil- and wax-containing solutions.

Many scientists (Brown et al. 1994; Pauly et al. 2001, 2003; Li and Gong 2010; Struchkov and Rogachev 2014) shown both for live oil at constant composition and for degassed oil that WAT of waxy oil linearly increases with increase in pressure. Pan et al. (1997) shown composition effect on wax precipitation: An increase in concentration of light components in oil leads to decrease in WAT.

According to certain studies (Turkulov et al. 1986; Paso et al. 2009; Kasumu et al. 2013; Struchkov and Rogachev 2016) WAT decreases with increase in cooling rate. Scientists explain this phenomenon with various kinetics of wax nucleation and crystallization.

Nowadays, researchers find convenient to describe the whole variety of disperse systems combinations using all technologic tool available, as well as to identify the role of each system element individually to change its properties. So, the authors modeled and investigated simplified systems that were wax-containing solutions. This paper is dedicated to study of influence of various parameters to WAT in model systems. These tests were carried out via visual and rheological methods.

Laboratory equipment and fluid samples

Laboratory equipment

WAT in model hydrocarbon systems by visual method under high-pressure/high-temperature (HP/HT) conditions was estimated via the PVT-measuring (pressure, volume, temperature) system. Schematic diagram of the experimental unit shown in Fig. 1. The basic components of the laboratory equipment are as follows: The high-pressure cell (PVT-cell) with the observation window placed inside the air bath (air oven) that maintains appropriate temperature pre-set by the researcher; pump (P) that maintains constant pressure inside the cell through the test; microscope (M) that records micrographs of the fluid sample and valves (V1, V2).

In addition, rheological method using plate rheometer under ambient pressure was presented to match visual method.

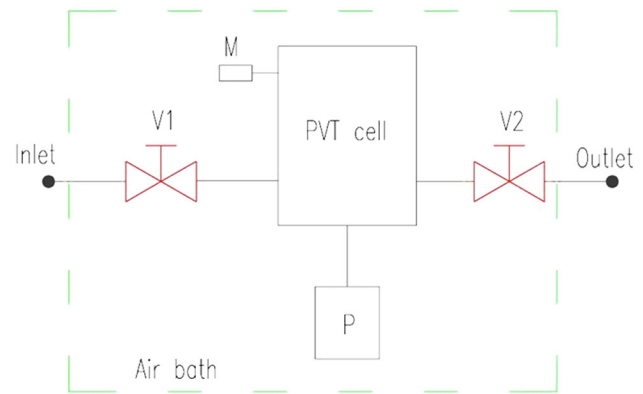


Fig. 1 Schematic diagram of PVT-measuring system. *P* pump, *V* valve, *M* microscope

Properties of model solutions

Six model hydrocarbon systems (model solutions) were wax (52–54 °C m.p.) in kerosene solutions. Concentration of wax in model solutions varied between 10–60 % by weight in increments of 10 wt%.

Experimental procedure

WAT determination in model solutions by visual method under HP/HT conditions

- The PVT-cell with bulk volume of 30 ml heated to temperature of 70 °C was vacuumized and filled up with model solution pre-heated to temperature at which wax is completely dissolved in kerosene (60–70 °C) under ambient pressure.
- Then, pressure inside the cell was increased up to 35–40 MPa by the pump, and the experimental system was kept under these thermobaric conditions for 30 min.
- Then, the cell was cooled down to 10 °C below WAT under isobaric mode at initial maximum pressure (35–40 MPa) and cooling rate of 0.042 °C/s. Temperature at which the first wax crystal appeared in model solution (WAT) was determined due to the micrographs of the sample recorded by microscope (one data point of WAT for one experiment).
- Then, temperature of solution was increased up to 70 °C again, pressure was reduced to the following step (five values of pressure were set) and the system was thermostated at new thermobaric conditions for 30 min. New experiment was performed upon complete dilution of wax in model solution.
- As a result, five data points of WAT at varied pressure for one concentration of wax in model solution are obtained.

- Experimental unit was carefully washed at high temperature by paraffin solvent and dried.
- Then, model solution with higher wax concentration was prepared and experiment was repeated.

WAT determination in model solutions under ambient pressure by rheological method

Experimental conditions of rheological test for model solutions are as follows: laminar steady-state flow, no slippage, homogeneity of samples and no chemical changes in the sample.

- Required volume of a test sample was put on a measuring plate.
- The following experimental conditions were set: gap of the measuring system plate-to-plate was 0.4 mm, shear rate was 10 s^{-1} and cooling rate was $0.042 \text{ }^\circ\text{C/s}$.
- Then, experiment was carried out on the sample temperature-controlled over a period of 10 min under temperature of $70 \text{ }^\circ\text{C}$. A layer of the model solution was cooled in gap of the measuring system at temperature from 70 to $10 \text{ }^\circ\text{C}$ below WAT. During the experiment, solution was heated and cooled using a Peltier element.
- The measuring system was carefully cleaned and dried after the end of experiment. Then, other sample was put on a measuring plate, and the following experiment was carried out.

As a result, dependence of shear stress on shear rate for a certain temperature under ambient pressure and dependence of effective viscosity of solution on temperature under ambient pressure were obtained. The sharp viscosity-temperature curve break attends to WAT. Wax crystallization in solution leads to sharp increase in effective viscosity and shear stress due to formation of the spatial structure of wax. Influence of various external factors on WAT was evaluated.

Impact of pressure and concentration of wax dissolved in model systems on WAT

The study was carried out by visual method. Figure 2 shows obtained test results.

Wax appearance curves for model solutions were obtained of the form as follows:

$$P = P^* + k * \ln\left(\frac{WAT}{WAT^*}\right), \tag{1}$$

where P^* ambient pressure, MPa; WAT^* wax appearance temperature in the model under ambient pressure, $^\circ\text{C}$; WAT

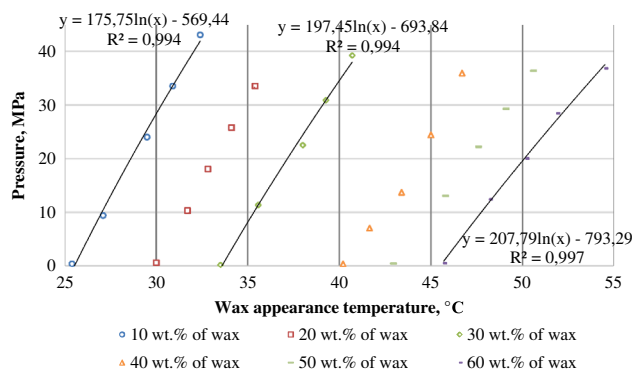


Fig. 2 Dependence of pressure on WAT for various wax concentration in solutions (wax appearance curves)

wax appearance temperature in the model under pressure P , $^\circ\text{C}$; k a constant of the phase change in the Clapeyron–Clausius equation, to that wax crystallization in model solutions may be conveniently related to.

Obtained data are completely confirmed by the Clapeyron–Clausius equation, describing first-order phase transitions (Sharma 2001). Increase in WAT resulting from increase in pressure is related to the greater regularity of the system, meaning reduction in its entropy, rising in packing density of wax molecules in solution, and shortage in length of their free path, which are responsible for stronger influence of diffusion of wax molecules promoting crystallization.

It is understood from Eq. 1 that:

$$WAT = WAT^* * \exp\left(\frac{P - P^*}{k}\right), \tag{2}$$

Dependence of WAT in solution on wax concentration and pressure is obtained based on following conditions: Pressure was $0.1\text{--}40 \text{ MPa}$ and wax concentration was $10\text{--}60 \%$ by weight:

$$WAT = [39.25 * C + 21.65] * \exp\left(\frac{P}{175.75}\right), \tag{3}$$

where C concentration of dissolved wax in model solution.

Thus, increase in pressure and concentration of wax-containing solution leads to rise in WAT in model system.

Impact of wax concentration in model solutions and addition of mechanical impurities on WAT

All further studies were conducted by rheological method under ambient pressure via rheometer with the measuring system plate-to-plate.

The obtained WAT data are comparable to results from visual method. Comparison of investigation methods

showed a difference in measured WAT in model systems an average of 1.1 °C (Fig. 3).

When using visual research method, temperature under which the measuring system register appearance of the first crystal of wax in solution (sensitivity limit of the research equipment of 1 micron) is accepted as WAT. Data points in Fig. 3 (for rheological method) correspond to effective viscosity-temperature curve breaks. Data points in Fig. 3 (for visual method) correspond to appearance of solid wax particles in model solution obtained by micrographs. When performing rheological test, temperature is accepted as such at which the break of a curve for effective viscosity of solution versus temperature $\mu = f(T)$ is observed (Fig. 4). Viscosity growth during the experiment is due to the beginning of the solid phase nucleating seeds in solution and fluctuation contacts of mixed up macromolecules of wax of bound layers moving at different velocity in gap of the measuring system as decrease in temperature. However, not every measuring system is able to detect negligible changes of the system rheological properties at high precision. This is responsible for difference in measured values of WAT in model systems using two methods.

Kaolinite in concentration of 2 g/l was added to pure wax-containing solution, and parallel experiments for both pure solution and solution with addition of kaolinite under identical conditions were carried out. Addition of mechanical impurities to the tested system results in disruption of the phase equilibrium of dissolved wax in solution and early wax crystallization (Fig. 7). Thus, the measuring system identifies the early increase in viscosity of mixture which the authors relate to WAT in solution (Fig. 4). Heterogeneous nucleation (providing that there are any free surfaces of solid particles) is more favorable process in terms of thermodynamic properties compared to homogeneous nucleation of the new phase in bulk solution in absence of solid particles (Pantell and Puthoff 1969).

Consistency curves of model wax-containing solutions for different temperature are shown in Fig. 5.

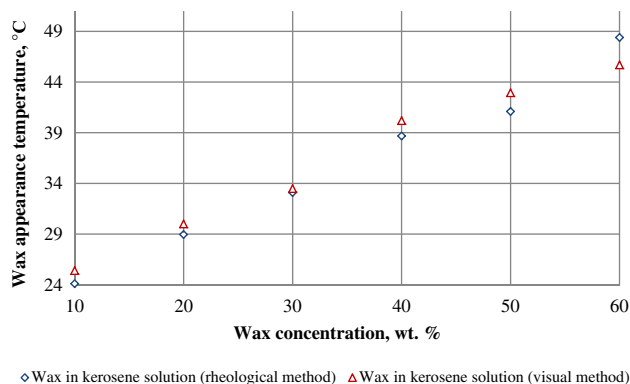


Fig. 3 Dependence of WAT in solution on wax concentration (visual and rheological methods)

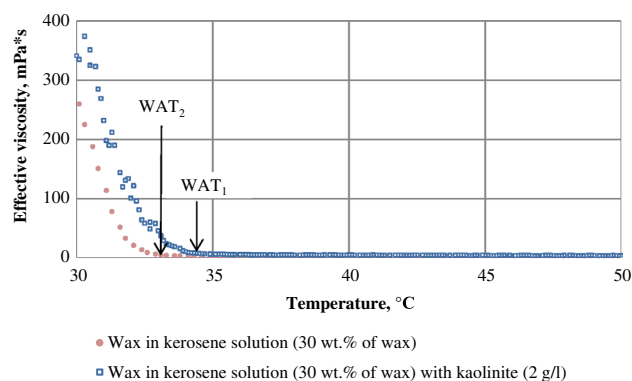


Fig. 4 Dependence of effective viscosity of solution on temperature (pure solution and solution with addition of kaolinite)

Consistency curve of wax-containing solution under 50 °C is little different from the same of Newtonian fluid (Fig. 5). However, upon reaching WAT in model, the coagulated structure appears in it with the dispersed phase represented by the solid wax crystals. Hereat, the range of fluid shear rate of 0–12 s⁻¹ is characterized by the initial destruction of covalent bonds between atoms of bound wax molecules in crystals and orientation of separated solid particles toward the flow direction. When reaching shear stress of 351 MPa, solution starts flowing with the maximum destructed structure (the range of shear rate of 12–40 s⁻¹). Addition of mechanical impurities into research systems provides multiple increases in shear stress and energy of thixotropic destruction of formed structures.

Mathematical relation of WAT in model solutions on wax concentration is obtained using rheological method (Fig. 6):

$$\text{WAT} = 0.4671 * C + 19.373, \quad (4)$$

where C wax concentration in model solution, % by weight.

Influence of mechanical impurities nature on WAT was evaluated. The test results are shown in Table 1.

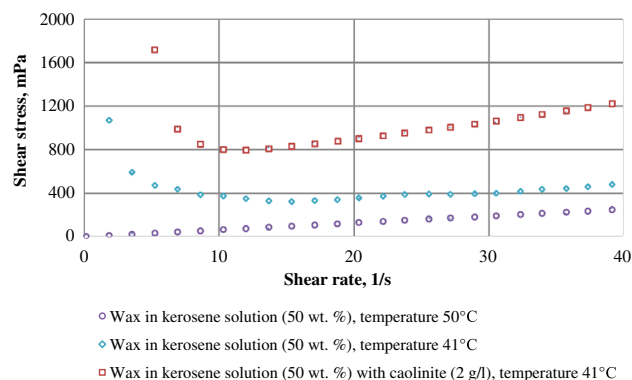


Fig. 5 Dependence of shear stress on shear rate (consistency curves of model solutions)

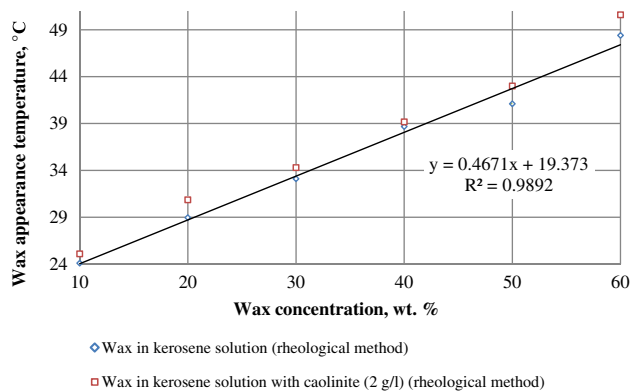


Fig. 6 Dependence of WAT in solution on wax concentration

Table 1 Influence of addition of mechanical impurities to model solutions on WAT

Origin of mechanical impurities	Concentration of mechanical impurities (g/l)	Wax appearance temperature (°C)
–	–	33.1
Calcite	2	36.4
	1	36.5
	0.25	36.1
Sandstone	2	35.9
	1	35.7
	0.25	35.8
Kaolinite	2	34.3
	1	34.4
	0.25	34.1

The particle size of mechanical impurities presented was not >0.1 mm, and gap in the measuring system plate-to-plate was set at 0.4 mm. The sensitivity of the measuring device with addition of mechanical impurities of the same origin in different concentrations (0.25–2 g/l) to the model solutions does not allow identifying significant changes in its rheological parameters, and this specifies similar value of WAT. However, mineral composition of solid particles influence on parameters to be measured in different degrees. The nature of this effect on properties of model system will be primarily determined by the state of free surface of particles and their sizes. Activated surface (mechanical, magnetic, chemical treatment, etc.) of foreign particles in crude, in the opinion of the authors, could increase in WAT in oil, compared to untreated surface.

Conditions of wax crystallization in wax-containing solutions are similar to wax crystallization in crude oil. Like asphaltenes, mechanical impurities initiate the snowballing process of wax precipitation due to recession in critical increment of energy to perform the phase change of wax molecules. So, asphaltenes that is the finely divided

phase uniformly dispersed in the bulk of crude oil reduce value of WAT (Kriz and Andersen 2005) to the certain threshold ratio of asphaltene/resin (A/R) acting as the multiple crystallization seeds of wax. Reallocating between solid particles of asphaltenes, wax starts to form the crystalline chain in volume, forming a structure of primarily coagulation-crystallization type. However, with the shortage of resins in oil, asphaltenes proceed coagulating, the solid particles grow in size and the number of crystallization seeds rapidly drops followed by reduction in free surface area. Wax molecules are adsorbed onto the surface, resulting in that newly formed aggregates appear in the sensitivity area of measuring tools earlier which is the reason to explain an increase in WAT in crude oil. Comparison of these two cases is reasonable at the similar dynamics of the solid phase formation in crude oil.

Impact of the measurement system gap on WAT

Experiment requirements: shear rate was 10 s^{-1} , cooling rate was 0.042 °C/s . Solution was investigated at wax concentration of 30 % by weight. The measurement system gap (z) increased stepwise upon each test within the range of 0.02–1 mm. A new portion of model solution was used in each subsequent test.

The test results are shown in Fig. 7.

The result of the Clapeyron–Clausius equation is the following:

$$\Delta S = \frac{L_{12}}{WAT}, \tag{5}$$

where $\Delta S = \Delta s * N$ change in the system entropy that presents N molecules with the phase change, Δs the same for a single molecule, WAT absolute temperature of the phase change, $L_{12} = l_{12} * N$ latent heat of the phase change

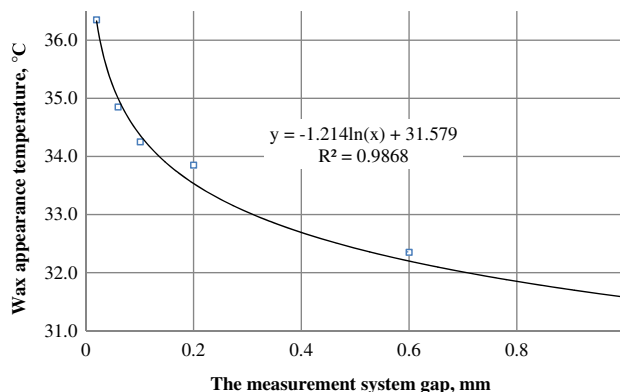


Fig. 7 Dependence of WAT in solution on gap of the measuring system

of the certain amount of substance at this temperature, l_{12} the same for a single molecule.

In passing to microstates of the system, Eq. (5) is transformed as follows:

$$\text{WAT} * \Delta s = l_{12} = \text{const.} \quad (6)$$

It can be seen from Eq. (6) that any change in the entropy of the system consisting of a single molecule will result in change of the phase transition temperature.

Decrease in size of the measuring system gap (z) plate-to-plate causes an increase in WAT in model solution (Fig. 7). With decrease in z , a smaller volume of solution is used in the test and, accordingly, the minimum number of wax molecules which is a more regular system. Therefore, according to Eq. (5) L_{12} and ΔS of the system decrease, but to different extent. An increase in WAT is assumed to be responsible for additional decrease in entropy of model solution in the course of transition from one thermodynamic macrostate to another due to reduction in the number of microstates that characterize the system (solution) in the whole.

As it is known, entropy is a measure of disorder. If smaller quantity of sample takes part in measurements, then sample has smaller entropy, and solution has fewer possible configurations of the individual wax molecules so that any thermodynamic process (particularly, phase transition in solution) has high probability. In this case, one of the key parameters is inertance of system. It is known that wax crystallization carried out with the release of heat and this process took some prolonged period. Experimental conditions change spontaneously with change in quantity of the studied sample. Particularly, decrease in volume of solution (decrease in gap of the measuring system) leads to decrease in its general thermal capacity. Consequently, time for transfer of heat from a sample to environment decreases (and also time which requires to crystallization of all wax molecules decreases) at identical cooling rate. Therefore, the measurement system detects the wax crystallization onset at higher temperature.

Impact of cooling rate on WAT

Since nucleation is the forced stage of the crystallization process, and the additional external energy is required to form free surface of a new phase, it is potential only under some subcooling of the system (solution) that is $\Delta T = \text{WAT} - T$. The minimum size of the nucleus, where it is sustainable and capable to further growth is calculated based on relation (Pantell and Puthoff 1969).

$$r_{\text{critical}} = \frac{2 * \sigma * \text{WAT}}{L_v * \Delta T} \quad (7)$$

where L_v molecular heat of the phase change, σ the interfacial surface tension.

As it is seen from Eq. (7), increase in subcooling degree of the system facilitates reduction in the critical size of nucleus of the new solid phase, which results in increase in probability of their formation.

Cooling rate during the experiment was calculated according to relative parameters of oil production based on the following considerations: velocity of upwardly flowing oil stream through tubing $v = \frac{Q}{F} = \frac{4 * Q}{\pi * D^2}$, m/s; where Q flowrate, m^3/day ; F cross-section area of the inner diameter of tubing, m^2 ; D diameter of tubing, m. Duration of the test was corresponding to time of oil lifting from the bottom-hole to the well head $t = \frac{H}{v}$, sec; when cooled, from the downhole temperature to the well head temperature $\Delta T = T_{\text{dh}} - T_{\text{wh}}$, °C; where H well depth, m; T_{dh} , T_{wh} downhole temperature and well head temperature, accordingly, °C. The calculations were based on operation conditions for one of producing wells of oil fields in Samara region complicated with formation of asphaltene-resin-paraffin deposits on the downhole equipment and flowlines. $D = 0.062$ m, $Q = 20\text{--}120$ m^3/day , $H = 1990$ m, $\Delta T = 30$ °C (average value). WAT in model system was determined similarly to that used in the previous studies by rheological method under ambient pressure. Experiment requirements: gap was 0.4 mm, shear rate was 10 s^{-1} , and wax concentration in solution was 30 % by weight. The test results are shown in Fig. 8.

The obtained dependence is adequately described by the function (8).

$$\text{WAT} = -0.739 * \ln\left(\frac{\Delta T}{\Delta t}\right) + 31.141. \quad (8)$$

At high cooling rate, the studied system (model solution) is over cooled and wax does not form solid

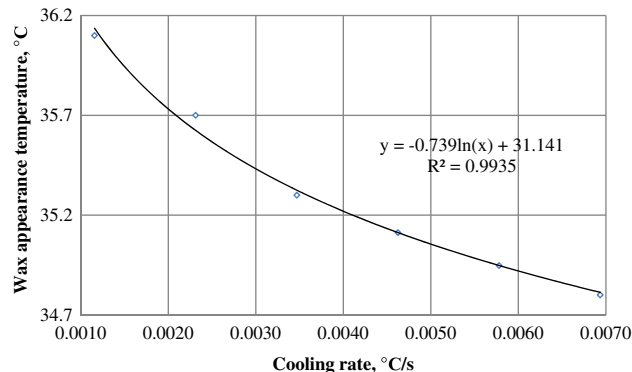


Fig. 8 Dependence of WAT in solution on cooling rate

phase yet, while its later crystallization from model solution is reported, and thus the inertance of the tested system is shown. Moreover, multiple stable nucleation seeds of smaller sizes are form that is the centers for subsequent crystallization of wax.

Impact of shear rate on WAT

Figure 9 shows dependence of WAT in model solution on shear rate. Test requirements: gap was 1 mm, cooling rate was 0.042 °C/s, wax concentration in model solution was 30 % by weight.

Increase in shear rate within the range of 0.5–10 s⁻¹ facilitates an increase in WAT in solution (Fig. 9). This occurrence may arise from that increase in shear rate may lead to expansion of vertical diffusion of wax molecules performing consistent feeding of growing crystals with the building material (wax molecules) and the transition to the diffusion-kinetic crystallization behavior. With the further increase in shear rate of the solution layers relative to each other (10–100 s⁻¹), difference of kinetic energy of wax molecules in bound micro-flows exceeds the energy of covalent bonds intended to aggregate them and no significant increase in WAT is reported.

Shear rate of layers of oil in relative positions in flow also is important role for the waxing process of wells. Shear rate directly depends on well flow rate. With its increase up to certain values, the depth of organic deposition moves towards the wellhead due to excess of shear stress in flow upon adhesion of the formed solid organic matters to the surface of tubing (Jennings and Weispfennig 2005). However, further increase in well flowrate results in the intensive mixing of layers of oil (as the result of the change in the flow condition), the mass transfer per unit time increases, and at the same time the dynamics of solid organic compounds to form in oil strengthens accelerating the process of the downhole equipment waxing (Jennings and Weispfennig 2005). Thus, the slightest change in

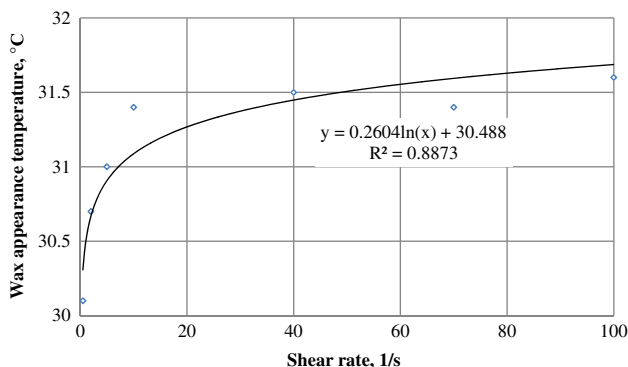


Fig. 9 Dependence of WAT in solution on shear rate

production conditions will definitely affect changes in properties of the whole production system.

Impact of watercut of solution and addition of mechanical impurities on WAT

Under preparation emulsions, the emulsifier of water-in-oil emulsions Yalan was added to hydrocarbon phase of watercut mixture at concentration as calculated by the following equation:

$$w_e = w_e^* * \frac{1}{1 - k}, \tag{9}$$

where w_e^* concentration of the emulsifier in hydrocarbon phase of mixture, unit fraction; k distribution coefficient of the emulsifier Yalan between aqueous and hydrocarbon phases, unit fraction.

The following values were used for testing: $k = 0.06$, unit fraction, $w_e^* = 0.01$ unit fraction.

Distribution coefficient of Yalan between phases was taken into account to ensure similar concentration of the surface active substance in hydrocarbon phase with varying watercut of mixtures and, consequently, at their equivalent effect on wax molecules.

Emulsions were prepared using a laboratory propeller type mixer at mixing rate of 3000 rpm for 40 min under ambient temperature of 25 °C. Test requirements: shear rate was 10 s⁻¹, watercut was 10–90 % in increment of 10 %, cooling rate was 0.042 °C/s, gap of the measuring system was 0.4 mm. The wax-containing solution (wax concentration of 10 % by weight) was investigated. Curves $\mu = f(T)$ for watercut systems are shown in Fig. 10.

In this case, mechanical impurities give rise to increase in viscosity and WAT.

Hysteresis loop shown in consistency curves for watercut wax-containing solution (Fig. 11) under 50 °C describes the system as the pseudoplastic system having

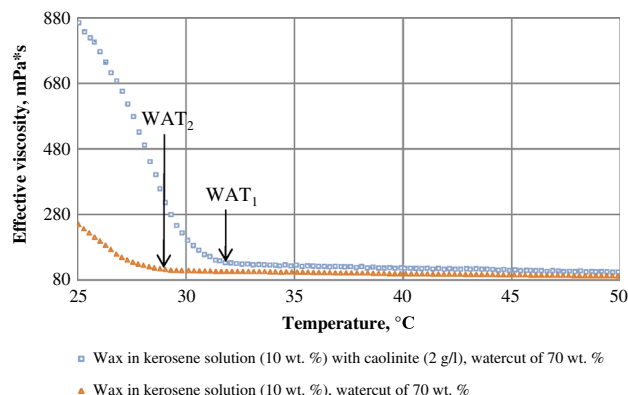


Fig. 10 Dependence of effective viscosity of solutions on temperature

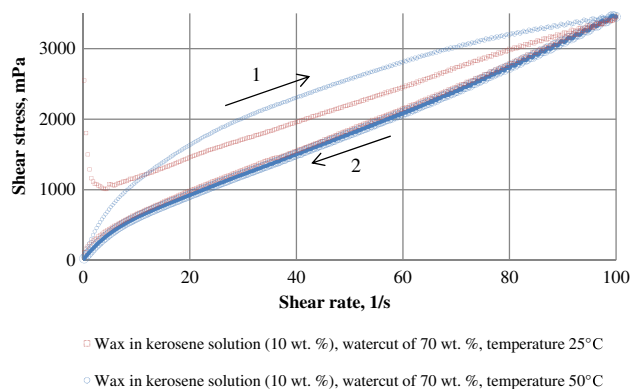


Fig. 11 Dependence of shear stress on shear rate at various temperatures (consistency curves of watercut model solutions)

thixotropic properties typical to coagulation structures. This may be related to rise of water droplets dispersity with increase in shear rate (upward curve trend) and to low-velocity water droplets coalescence with decrease in shear rate (downward curve trend). As in the case of waterless systems, decrease in temperature of watercut model solutions below WAT leads to the phase transition of wax and appearance of the structure having initial shear stress. Narrowing of hysteresis loop under 25 °C (Fig. 11) gives evidence that degree of the system thixotropy decreases and structure changes to stable system with reaching thixotropic properties. In other words, appearance of three-dimensional structure recovers quickly in time.

With increase in watercut of model solutions both WAT and viscosity increase (Table 2).

Figure 12 shows micrographs of prepared emulsions (magnification of 10).

Increase in WAT with growth of watercut of wax-containing solutions, in the opinion of the authors, is caused by:

- sensitivity of research equipment to shear stress. Viscosity and shear stress are small at low watercut, and the measuring system hardly determines initial slightest increase in these parameters induced by wax crystallization, whereas, the clearer break point of $\mu = f(T)$ is reported with rise in watercut;
- inhibiting tubes of water droplets get thin and crystallization-coagulation structure forms much faster in time due to reduced amount of hydrocarbon phase (with increase in watercut).

Figure 13 shows three areas within WAT increases near-linearly with growth in watercut: I—area of watercut in the model system at which emulsion breaks for 10 min, II—emulsion breaks for an hour, III—emulsion breaks for a day.

However, the production conditions of oil show dual nature of impact of watercut on formation of asphaltene-resin-paraffin deposits in well. On the one hand, increase in watercut of mixture increases total heat capacity of upstream, which promotes to raise temperature at the wellhead. This reduces temperature gradients between the bottomhole and wellhead and decreases kinetics of wax precipitation. At the higher watercut (up to 60 % by weight), water performs as the external phase separating oil from surface of tubing and changes the steel surface from oil wet to water wet. In that case, solid asphaltene-resin-paraffin particles being formed in volume do not deposit onto surface of the downhole equipment. This is the case for the oil-in-water emulsion only. On the other hand, in case of formation of water-in-oil emulsions, the inhibiting tubes of water droplets presented by natural surface active agents (surfactants), strengthened with three-dimensional structure of wax adhere to the wellbore surface in accordance with its larger free surface and high adhesion factors forming organic deposits that are hard to remediate.

Table 2 Influence of watercut and addition of mechanical impurities on WAT and effective viscosity

Watercut (wt%)	Wax appearance temperature (°C)		Effective viscosity at 40 °C (MPa s)	
	Without mechanical impurities	With addition of kaolinite 2 g/l	Without mechanical impurities	With addition of kaolinite 2 g/l
0	24.1	25.1	2.8	3.5
10	24.3	25.5	2	2
20	24.5	26.0	3	3
30	27.3	28.3	6	7
40	28.0	29.0	15	16
50	28.2	29.6	30	35
60	28.6	29.8	72	77
70	29.6	32.1	100	116
80	30.8	33.6	231	368
90	34.1	35.1	429	828

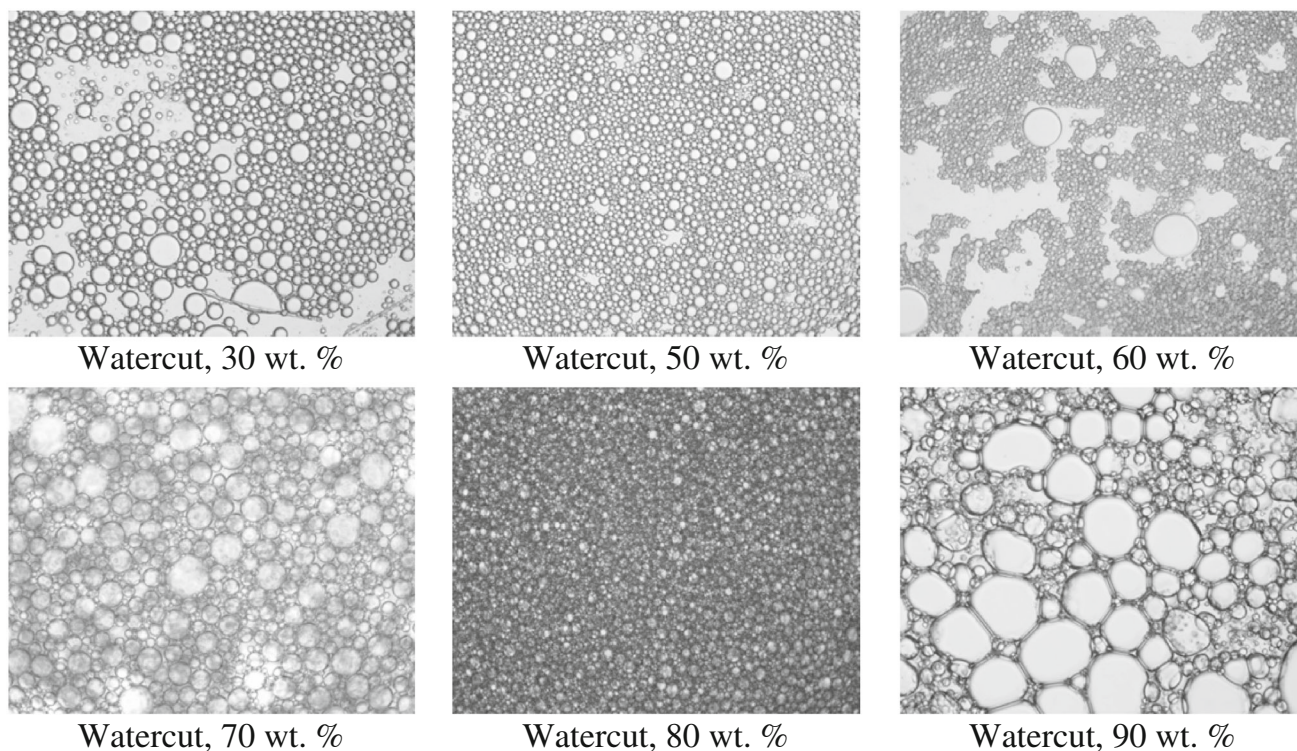


Fig. 12 Micrographs of emulsions of wax-containing solutions at various watercut

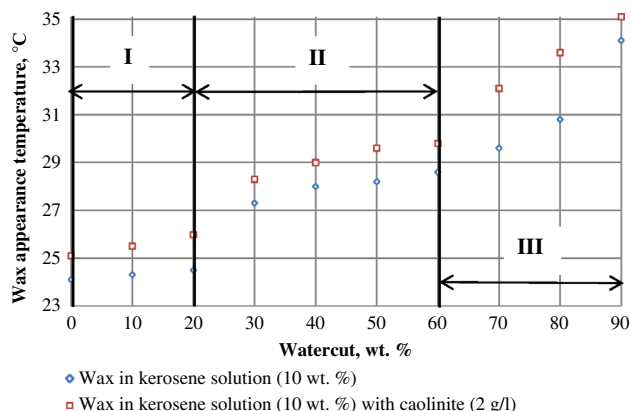


Fig. 13 Dependence of WAT in solution on watercut (pure wax-containing solution and solution with addition of kaolinite)

Impact of addition of chemical compositions to model solutions on WAT

The test conditions were as follows: Shear rate was 10 s^{-1} , cooling rate was $0.042\text{ }^\circ\text{C/s}$, gap of the measuring system plate-to-plate was 0.4 mm. Wax inhibitors at concentration of 1 % by weight presenting the composite mixture of surface active substances in organic solvents were added to model wax-containing solutions (wax concentration of 30 % by weight). The test results are shown in Table 3.

Table 3 Influence of addition of wax inhibitors to oil on WAT

Wax inhibitors	Wax appearance temperature (°C)
–	33.1
Ekowinter	32.3
SNPCh-7941	32.0
SNPCh-7912	32.3
SNPCh-7909	31.8
RKD	32.0
Union 3000	32.1
Glaid	32.6
Designed inhibitor	32.5

Wax inhibitors added to solutions reduce WAT to various extent

Wax inhibitor SNPCh-7909 (Fig. 14) showed the greatest efficiency on model solutions. Nonionic surfactant designed by the authors that is the product of reaction between unsaturated fatty acids and ethyleneamine ester, aminoalcohols (active basis) in organic solvent also showed satisfactory results (Table 3). The authors assume that the reported decrease in WAT in solution may be dependent on the high surface activity of reagents that may be responsible for decrease in surface tension at the boundary solution—solid particles and corresponding reduction in the minimum size of the nucleus according to

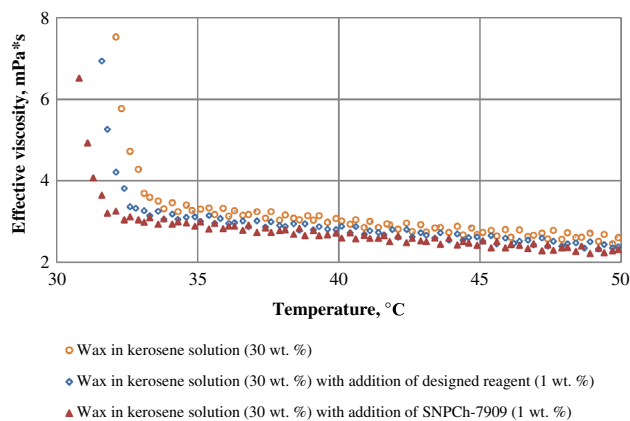


Fig. 14 Dependence of effective viscosity of solutions on temperature (pure solution and solution with addition of inhibitors)

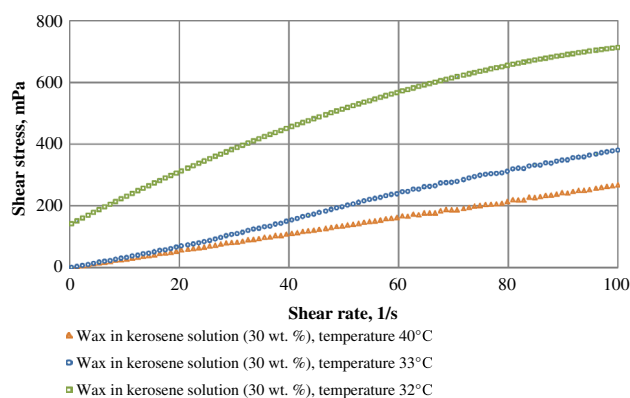


Fig. 15 Dependence of shear stress on shear rate (consistency curves of model solution with addition of Ekowinter inhibitor)

Eq. (7). The authors also assume that such activity of inhibitors may facilitate slow-down in kinetics of wax precipitation.

The absence of the initial reduction area of shear stress (Fig. 15) with increase in shear rate (when temperature reaches WAT) may indicate that Ekowinter has a depressor action in relation to wax, and presumably in such conditions the coagulation structure is formed (soft deposits). Under this temperature and wax concentration in solution with added reagent, structure can hardly reach sufficient density, and it wastes at lower shear stress.

Conclusions

In this study, the authors investigated impact of various parameters on WAT in wax-containing solutions, and following relations were obtained:

1. With increase in pressure WAT in solution rises. This is caused by solidifying of the paraffin hydrocarbons packing in solution and increasing action of diffusion

processes during waxing. Distance between the closely spaced wax molecules in solution decreases, and wax crystals are fed with the building material (wax molecules) more steadily.

2. Free surface in solution presented with mechanical impurities of different origin gives rise to WAT. Impurities act as the additional wax nucleation seeds, and it causes solidifying the crystalline structure and increase in viscosity of solution and shear stress.
3. Decrease in gap of the measuring system plate-to-plate brings to growth in WAT in model solutions. This phenomenon is presumably associated with change of macrostates of the tested system and change in its entropy.
4. Increase in cooling rate causes increase in the extent of subcooling degree of solution and reduction in WAT, which characterizes its inertance. Wax crystallization takes particular time. New portion of wax does not crystallize as fast as solution is cooled.
5. WAT rises with increase in shear rate which can be induced by the vertical mass transfer of the building material (wax molecules).
6. Increase in watercut of model solutions gives rise to WAT that may be caused by thinning of the water droplets inhibiting tubes presented as the wax-containing hydrocarbon phase. Driving force of early wax crystallization in solution is reduction of system entropy.
7. Addition of wax inhibitors to model solutions reduces WAT presumably due to the high surface activity of inhibitors causing depressor action on wax molecules. Inhibitors adsorb on small wax crystals, change their free surface, and prevent their further enlargement. Inhibitors reduce an interfacial tension on border solution—solid wax particles, reduce the minimum critical sizes of solid wax particles, the last appear in the sensitivity area of measuring tools at a later time. The most effective wax inhibitor is SNPCh-7909.

However, despite obtained dependence of WAT on various parameters for the prepared model wax-containing solutions, they will definitely decay in case of oil. All these factors will influence WAT in oil to the lesser extent as compared to wax-containing solutions due to presence of natural surfactants in oil (asphaltene and resins) that show additional depressor effect. Dependencies will be determined by influence these parameters on activity of asphaltene and resins in oil.

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