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Paraffin blockage specificsin model petroliferous systems

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Abstract

In this paper we study the effect of the temperature factor, the content and composition of the dispersed phase components: paraffinic hydrocarbons, resins and asphaltenes, – on the sedimentation process in model systems. Adding a 0.025 to 0.1 wt.% of resins and asphaltenes doping agent to a 20 wt.% paraffin wax solution in kerosene shall be optimalto resist precipitate formation. Asphaltene and resin compositions, derived from the methane-kind petroleum-oil, are characterized by a maximum ability to prevent sedimentation. The presence of resins and asphaltenes in a model system shall significantly affect the physical and chemical characteristics of the sediment.

1. Introduction

Under the influence of external factors, in the process of oil extraction and transportation, asphalt, resin and paraffin deposits (ARPDs) shall be precipitated and sorbed on the surface of the equipment. The ARPDs amount and composition shall be determined primarily with the oil dispersion phase and the external conditions such as temperature, pressure and hydrodynamic factors. The ARPDs formation mechanism in paraffin and high-grade paraffin oils, representing polymict inhomogeneous composition inequilibrium systems, is quite a complex one. Therefore, many authors study the crystallization of petroleum wax using model systems based on paraffin solutions without the addition of asphaltenes and resins[1-5].

The fact that the asphaltene molecules and molecular aggregates are effective paraffins nucleating agents shall be

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deemed irrefutable[1,3,6]. At the same time, there are conflicting opinions about the process of paraffins crystallization itself and the involvement of resins and asphaltenes in that process. The research findings[7-9] confirm, that the "asphaltene– paraffin" molecular complexes formation is due to intermolecular interactions. The initial-stage sub-microcrystalline wax stabilization can be attributed to the adsorption of asphaltenes and resins, which are natural inhibitors of paraffin at the crystal surfaces[10].

According to other authors[11,12], no reliable evidence of intermolecular interactions between "paraffins – resins" and "paraffins - asphaltenes"or of theirco-crystallization in oil has been established. The occurrence of resins and asphaltenes in the asphalt, resin, and paraffin deposits can be attributed to the conventional liquid petroleum occlusion in the paraffin crystallization phase.

In this paper we study the effect of the temperature factor, the content and make-up of the dispersed phase components: paraffinic hydrocarbons, resins and asphaltenes – on the sedimentation process in model systems.

2. Testing procedures subjects and methods

Testing procedures have been performed using model petroliferous systems consisting of 10 and 20 wt.%paraffin solution in kerosene with petroleum resins and asphaltenes doping agents derived frommethane-type crude oil (resinous-asphaltenicmaterials$_{met}$) andaromatic-type (resinous-asphaltenicmaterials$_{ar}$).

The asphaltenes and resins contents in the crude oil havebeen determined by adsorption chromatography on alumina compliance with the ASTM D2007, and the paraffinic hydrocarbons in compliance with the ASTM E1519.

Resins and asphaltenes have been introduced in 10 and 20 wt.% solutions of paraffin wax in the form of individual components and their compositions in concentrations close to the content of the dispersed phase in the gas condensates and highlywaxy low tar crude oil (0.5 to 2.5wt.%) samples.

Inhibition of paraffin sedimentation has been studied using a ″cold finger″laboratory installation, which models the paraffin sedimentation process in a pipeline[13,14]. The installation consists of a cooled steel rod placed in the oil sample to be analyzed at a temperature range varying from 30 to 70°C, while the rod temperature varied within the range of 15 to 30°C. The amount of paraffin wax deposited on the rod has been determined by a gravimetric method.

The composition of n-alkanes in the source paraffin and oil sludge has been analyzed by high-temperature gas liquid chromatography, using a ″Perkin-Elmer SIGMA 2B″chromatograph under the following conditions: thephase SE-52 capillary column length – 33 m, at a 4°/min temperature rate linear ramp starting from the initial temperature of 100°C up to 290°C.

The sediment melting point has been determined in compliance with the ASTM D87 and D127.

The sediment plastic viscosity and yield stress has been measured by a LVDVIII Ultra brand rotary rheometer(″Brookfield″company, USA) using a "cone-plate" type thermostatic cylindrical measuring system.Monitoring of parameters (temperature, shear rate, the frequency of measurements) has been performed using the RheoCalc specialized software program.

3. Discussion of results

The crystallization process of paraffinic hydrocarbons (PH) is influenced both by their content and the composition as well as the cooling rate, the petroliferous system temperature and the temperature of the cooled surface[15]. The existence of the "wall/environment" radial temperature gradient,which accounts for the dissolved paraffin particles displacement towards the tube wall, prompts the dissolved paraffin concentration gradient formation[16,17].

Fig.1 shows the temperature range and PH-in-kerosene solution concentration gradient effect on the amount of the precipitated sediment. At a 70/30°C temperature gradient and 10 wt.%PH concentration, a negligible amount of paraffin wax shall be precipitated in the solution.
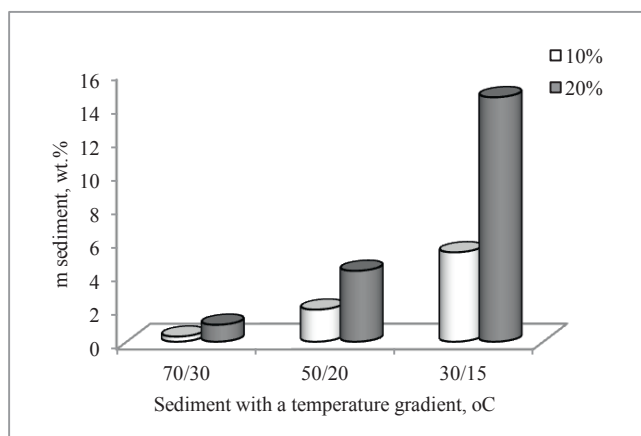
Fig.1. The effect of temperature gradient and the PH saturation of the solution on the amount of the precipitated sediment

As the temperature of the solution drops to 30 °C and that of the cooled surface goes down to 15 °C, both the intensity of precipitation and the amount of sludge produced shall be increased. This is due to the fact that the 70/30°C temperature gradient prompts precipitation of heat-resistant PH with a melting point at 57°C, only, while the bulk of the sediments having the melting point at 45°C shall be precipitated at 30/15°C, which is allocated the bulk sediment with a melting point 45°C, as, also, confirmed by the results of the n-paraffins gas chromatographic analysis. Therefore, further tests have been performed using sediment precipitated from a 20% PH solution having a 30/15°C temperature gradient.

The first stage of the research has been dedicated to studying the specifics of influence the resins and (methane- and aromatic-type) asphaltenes molecular structure, as well as their concentration produce on the PH crystallization. It has been shown that an introduction of 0.5 and 1 wt.% of asphaltenes (ASP), benzene (BRs) and alcohol-benzene resins (ABRs) of different nature in a 20% PH solution has resulted in a 40% reduction of the amount of sludge precipitation (Table 1).

Table 1. The effect of resinous-asphaltenic material components on the amount of sediment precipitated from a 20 wt.% PH solution, having a 30/15oC temperature gradient

RAM additives, wt.%	Amount of sediment precipitated from the solution, wt.%					
	RAM_{ar}			RAM_{met}		
	BR	ABR	Asphaltenes	BR	ABR	Asphaltenes
0	14.5	14.5	14.5	14.5	14.5	14.5
0.5	12.3	13.7	12.4	8.7	9.5	9.1
1.0	12.4	12.0	12.3	8.8	9.5	9.0
1.5	10.5	10.8	11.0	11.5	12.7	11.2
2.0	11.7	12.3	12.1	13.5	12.0	12.3
2.5	16.5	16.0	17.8	15.4	15.8	15.8

The methane-type RAM components have proved the most active; when added they prompt a maximum reduction in the amount of oil sludge precipitation. With further increase in RAM concentration, the amount of sediment precipitated in the solution begins to grow, and when a 2.5 wt.% doping agent is added, the inhibitory effect completely disappears. Thus, for a 20 wt.% PH solution in kerosene, a 0.025 ÷0.1 individual RAM component doping agent can be considered optimal in terms of resistance to the sludge formation.

The RAM ability to inhibit the precipitation process in a paraffin solution improves when RAM compositions are used to substitute specific resins and asphaltenes additives (Figure 2).
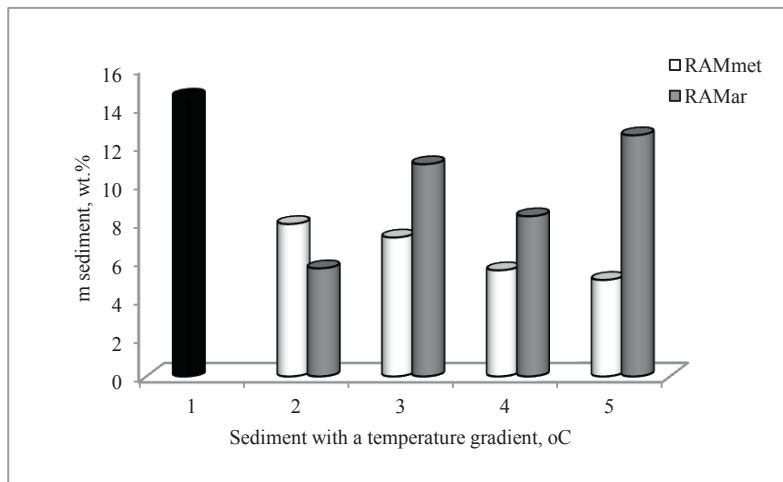
Fig. 2. Resinous-asphaltenic materials (RAMs) composition content and make-up impact in a 20% PH solution on the amount of the precipitated sludge: 1 – RAM-free; 2 – 0.5% BR + 0.5% ASP; 3 – 0.5% ABR + 0.5% ASP; 4 – 1% BR+ 0.5% ASP; 5 – 1% ABR+ 0.5% ASP

With the of benzene or alcohol-benzene resins mass fraction increase in the RAM composition up to 1 wt.%, we have observed a significant increase in inhibitory activity. The maximize ability to prevent sedimentation has been registered in RAM compositions of methane nature having a 1% BR + 0.5% ASP and 1% of ASF ABR + 0.5% ASP composition formulation, whose introduction into a paraffin solution reduces the amount of sediment by more than 2 times. That fact can be explained by the formation characterized by a certain ratio (in our study the resin/asphaltene ratio being 2: 1) of associates with enhanced surface activity.

It is reckoned that the structure of high-performance industrial paraffin inhibitors is such that one portion of the inhibitor molecules is cognate to petroliferous paraffinic hydrocarbons, while the other part comprises of polar groups. The most effective synthetic inhibitors are the ones which contain oxygen atoms in their structure. By analogy with synthetic inhibitors, the methane-type RAM efficiency shall be determined by high heteroatoms content in their structure, primarily represented by oxygen (5.9 wt.% - in benzene resins, 13.2 wt.% - in alcohol-benzene resins and 3.2wt.% - in asphaltenes) and the presence of alkene substituents. Increasing the RAM composition concentration in a solution up to 2 wt.%BR and ABR results in a reduced inhibitory effect.

The composition of individual n-alkanes sediments derived from solutions with a 30/15 $^{\circ}$C temperature gradient varies significantly dependent on specific added RAM components and their compositions. The molecular weight distribution of n-alkanes in a paraffin sample without RAM doping agents is of a mono-modal nature characterized by the C_{19}-C_{70} carbon number value with C_{25} having the maximum value. In paraffin-solution-sediments derived alkanes a bimodal distribution shall be observed with two distinct maxima in the C_8-C_{16} and C_{20}-C_{35} areas (Fig. 3. Addition of 1 wt.% of asphaltenes of aromatic nature to a 20% PH solution shall significantly alter the hydrocarbon ratio in C_8-C_{16} and C_{17}-C_{40} groups in sediment n-alkanes with an observed shift in the maximum n-alkane distribution towards lower molecular weights (Fig. 3).
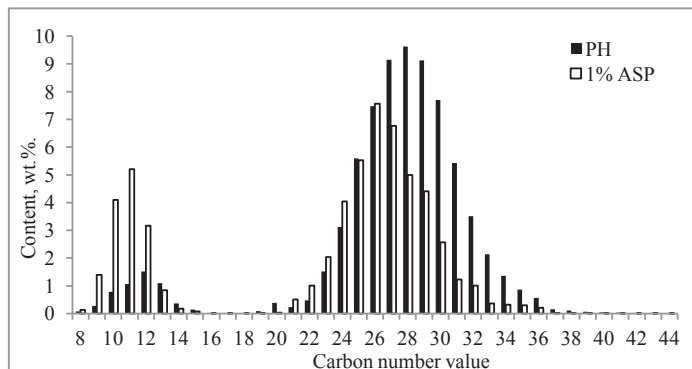
Fig. 3. The molecular weight distribution of sediment n-alkanes derived from a20% PH solution with no additives and with an addition of 1 wt.%of aromatic-type ASP

The paraffin crystallization processes in a solvent are mutually affected by low and high n-alkanes influence[18]. Low molecular weight n-alkanes can be integrated in the crystal structure of high molecular weight hydrocarbons, thus weakening intermolecular bonds and increasing the crystallization temperature.

Low molecular weight n- alkanes contained in sediments with an 8 to 16 carbon number value are an occluded kerosene fraction, which is a paraffin solvent. It is also known[19] that paraffin deposits often contain occluded mineral oil. Thus, only 7 to 14% of the deposits on the walls of the "Trans Alaska" pipeline belong to the solid phase while86 to 93% are represented by cleanoil.

The molecular weight distribution of n-alkanes in the sediments depends on the nature of the RAM compositions added to a PH solution. Thus, adding optimum (less than 1.5wt.%) concentration resin and aromatic nature asphaltenes shall increasethe ΣC_8-C_{16} n-alkanes fraction and reduce the ΣC_{17}-C_{40} fraction in comparison with the methane-nature compositions(Fig. 4, Table 2).
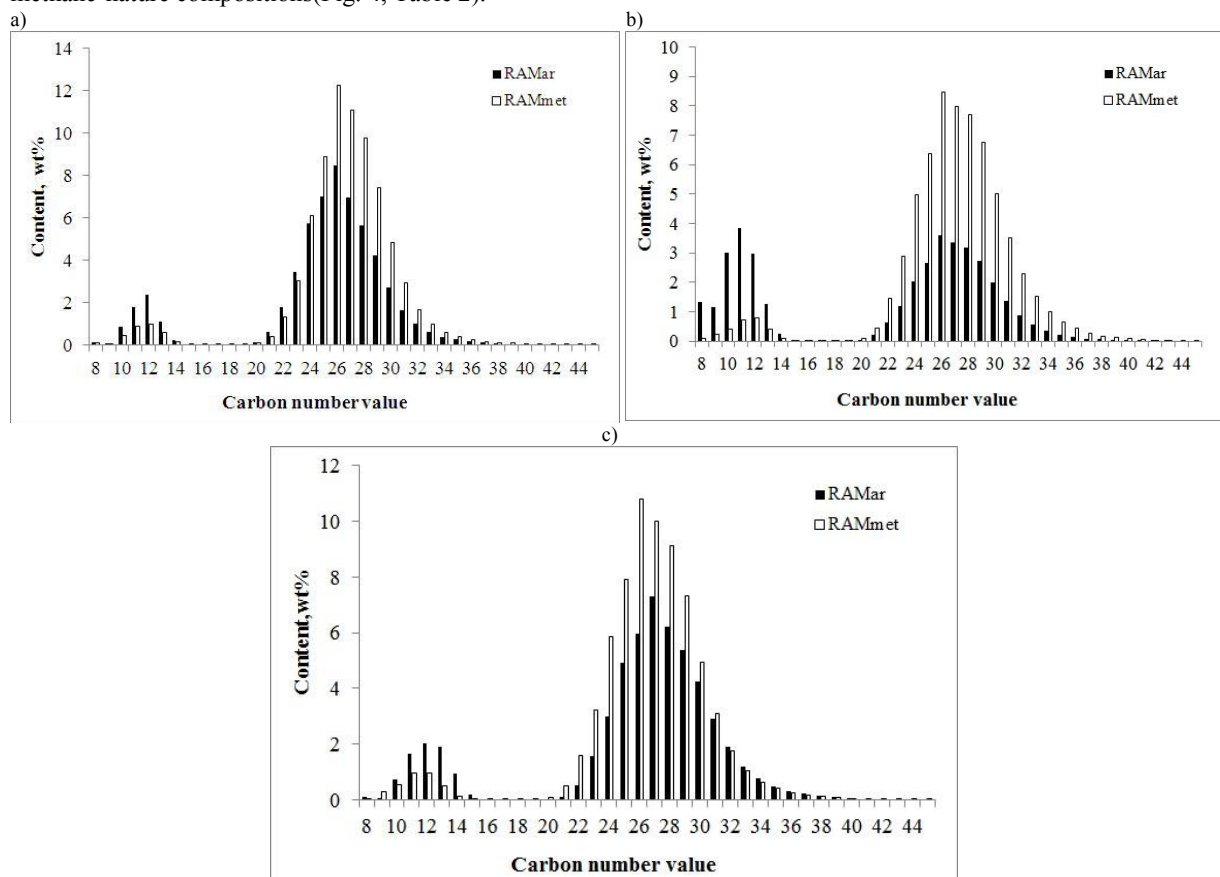
a)

b)

c)

Fig. 4. The molecular weight distribution of sediment n- alkanes, derived from a 20% PH solution with aromatic and methane types RAM additives : a) 1% ABR + 0.5% ASP; b) 0.5% BR + 0.5% ASP; c) 1% BR + 0.5% ASP

The analysis of table2 data onthe total content of ΣC_8-C_{16} and ΣC_{17}-C_{40} n-alkanes indicates that the sediment samples differ in the low and high molecular weight n-alkanes ratio values. The sediments separated from solutions with methane type RAM additives contain less C_8-C_{16} series n- alkanes. Their maximum number shall be observed in sediment obtained from a paraffin solution with asphaltenes additives.

Table 2. Content of ΣS_8-C_{16} and C_{40}-ΣS_{17} n-alkanes in sediments obtained from a PH solution with different types of RAM additives

Sediment samples obtained from a PH solution with RAM additives.	The n-alkanes content in the sediment, wt.%			
	RAM_ar.		RAM_met.	
	ΣC_8-C_{16}	ΣC_{17}-C_{40}	ΣC_8-C_{16}	ΣC_{17}-C_{40}
20% PH	5.3	68.1	5.3	68.1
1% BR	6.1	69.8	3.6	68.1
1% ABR	7.0	54.6	2.7	75.7
1% ASP	15.5	43.0	10.9	52.9
0.5% BR + 0.5% ASP	13.8	35.5	3.2	62.4
1% BR + 0.5% ASP	7.7	44.5	3.5	69.8
0.5% ABR + 0.5% ASP	8.2	52.2	6.5	66.9
1% ABR + 0.5% ASP	6.5	51.2	3.2	72.5

Sediments accumulate up to 30% benzene, 10% alcohol-benzene resins, and 80% asphaltene quantities of the total amount of respective RAM components in the source model solution.

The sediment components amount and composition shall determine their melting point T_{sm} (Table 3). The T_{sm} value increases with the increasing n-alkanes ratio and, conversely, decreases with increasing occluded liquid phase fraction. The T_{sm} maximum decrease shall beobserved in sediments obtained from solutions containing 1-2wt.% additives. ASPs characterized by the highest content of C_8 - C_{16} n-alkanes.

Table 3. The methane nature RAM components effect on the melting temperatureT_{sm} of sediments obtained from a solution with a 30/15 °C temperature gradient

Sediment samples obtained from a PH solution with RAM additives.	SedimentsT_{sm}, °C		
	BR	ABR	ASP
20% PH	45	45	45
0.5% RAM	42	37	37
1% RAM	27	21	19
2.0% RAM	22	20	18

The amount of occluded solution shall determine the porosity and toughness of paraffin deposits[19,20]. To compare the paraffin deposit toughness, the "yield stress" indicator shall be used, which characterizes the force to be applied to overcome the force of interaction between paraffin crystals to destroy the structure.

According to[20], the model paraffin system yield stress is exponentially dependent on the amount of paraffin wax. Adding asphaltenes to a model system shall reduce the temperature of gelation and the yield stress[21].

Table 4 shows the plastic viscosity and the yield stress values for sediments obtained from a 20 wt.% solution with a 30/15°C temperature gradient. RAM additives to a paraffinic model system shall significantly reduce the viscosity and toughness of precipitated sediments.

Table 4. The plastic viscosity and the yield stress of sediment obtained from a 20 wt.% paraffin solution

Model system	Plasticviscosity, mPa·s	Yieldstress, Pa
20% PH	145.8	4.2
1% BR	100.6	3.6
1% ABR	76.0	2.4
1% ASP	55.2	1.7

4. Conclusion

It has been found that the n-alkanes content and composition in sediment extracted from a paraffin model solution shall depend on the precipitation temperature conditions: lowering the temperature shall result in an increased low-melting hydrocarbon proportion in the sludge with the maximum molecular weight distribution shifted to the area with a smaller carbon number value. The sediment paraffin lattice has a solid crystalline structure, with the cells containing the liquid phase of the model system (kerosene). The presence of asphaltenes and resins in a model system shall change the ratio of the liquid and solid phases in the sediment. Lowering the proportion of the liquid phase shall increase the strength of the crystal lattice and, consequently, result in an increased viscosity of oil deposits.

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