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Temperature Dependent Behavior of Oil Dispersion System in Bulk and on the Metal Surface

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Abstract

This article focuses on the temperature dependent behavior of oil dispersion systems containing high amount of paraffins. In particular the properties of oils in bulk and during the contact with metal surface were evaluated by methods of rheoviscometry, thermal analysis, differential scanning calorimetry, gravimetry, polarization microscopy, gas chromatography and chemical analysis.

Analysis of rheological parameters of oil, morphology of paraffin crystals, and thermal properties at temperature interval between 0 - 90 ^{0}C allowed to determine the transition temperature of oil dispersion system from the molecular to free-dispersal and bounded-dispersal states. It was established that the indicated parameters depend on oil composition, molecular-mass distribution of paraffins, curing temperature and cooling rate.

Contacting of high paraffinic oils with steel surface leads to formation of asphaltene-resin-paraffin deposition (ARPD). The quantity, structure, composition and adhesiveness of ARPD depends on oil composition and gradient of temperature between heated oil and cooled metal surface. In case of temperature gradient is more than 30 ^{0}C the solid and high adhesive depositions are formed. Their structure is enriched by long chain high-melting paraffins. In case of temperature gradient is less than 20 ^{0}C, amorphous and easy removable depositions are formed. Their structures are enriched by mechanical admixtures, water, resin, asphaltene and low-melting short chain paraffins.

Key words: High-paraffinic oil; Oil dispersion system; Asphaltene-resin-paraffin depositions; Wax appearance temperature; Heat treatment

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INTRODUCTION

The peculiarities of structural change and state of oil dispersion system (ODS) in dependence of temperature are described in[1,2]. There are five different states of ODS which can appear during the heating: fixed disperse state (gel, jell), free disperse state (sol), conditionally molecular solute, free disperse state (sol) and fixed disperse state (gel, rigid foam). Transition stages of ODS are characterized by sharp change of shear stress on temperature. The most interesting states are the first three (from -20 to 100 ^{0}C) since they define the technological conditions of oil recovery, storage and refinement[2].

Due to different oil structure (composition and chemical nature) and variety of external affecting factors (pressure, temperature, solvent, additives, electromagnetic radiation), the majority of ODS researches were conducted on model systems, particularly in solutions of resin and asphaltene dissolved in hydrocarbons[3-6]. However, there are a few studies which are focused on structure and behavior of ODS in crude oil[2, 7-9].

Increased amount of paraffin in crude oil stimulates the interest of researchers to behavior of ODS with high contents of solid paraffins[10-12].

This paper is devoted to study the behavior of ODS containing high paraffin content before and after contacting with metal surface at temperature interval between 0 - 90 ^{0}C.

1. EXPERIMENTAL

1.1 Materials

Oil samples from fields of Kumkol, Akshabulak and Uzen were purchased in June, 2012 from the head part of oil pumping station.

1.2 Methods

The oil density was determined with the help of areometer in thermostate cylinders "Technoglass" (The Netherlands) according to MI 2153-2001.

The content of mechanical admixtures (C_{MA}) in oil was determined according to GOST 6370-83.

The content of water (C_W) in oil was determined using Dean-Stark apparatus according to GOST 2477-65.

The content of paraffin (C_P), asphaltene (C_A) and resin (C_R) in oil was determined according to GOST 11858-66.

Pour point (PP) of oil was determined using "S.D.M.-530" apparatus (Germany), according to ASTM D5853.

Kinematic viscosity (ν) was determined according to GOST 33-2000 with the help of capillary viscometer Ubbelohde. Apparent viscosity (η) and shearing stress (τ) at different shear rate (D) were measured by rotary rheoviscometer RHEOLAB QC of Anton Paar (Austria) with temperature control jacket LTD180, measuring system CC39/T200/XL/AL and measuring capsule C-CC39/T200/XL/AL. The values of stress limit (τ_0) were calculated from the Gershel – Balkli equation.

Formation of ARPD was examined by "cold finger" method according to methodology[17].

Shape and size of paraffin crystals were studied by Linkam Hot Stage apparatus (The Netherlands).

Wax appearance temperature (WAT), wax disappearance temperature (WDT) and enthalpy of these processes were determined by DSC Eva Setaram (France) at heating and cooling rate of 1 ^{0}C·min^{-1}.

Chromatographic analysis of oil samples was performed by gas chromotograph AutoSustemLX, model 3012 SIMDIS according to ASTM D2887.

2. RESULTS AND DISCUSSION

2.1 Composition and Physical - Chemical Characteristics of Highly Paraffin Oils

Composition (content of paraffin (C_P), asphaltene (C_A) and resin (C_R)) and main physical–chemical characteristics of oils from Akshabulak, Kumkol and Uzen oilfields containing high content of paraffin are presented in Table 1. The density (ρ_0) and pour point (PP) of oils decrease in the order of Uzen, Akshabulak and Kumkol oilfields (Western Kazakhstan). The value of PP that is responsible for the transfer of oil from free-dispersal to bounded-dispersal states is maximal for Uzen oil due to high content of paraffin.

Table 1
Composition and Physical-Chemical Characteristics of Kumkol (1), Akshabulak (2) and Uzen (3) Oils

Number #	ρ_0, kg/м^3	PP, ^{0}C	ν, mm^2/s at 40 ^{0}C	η, Pa·s at 20 ^{0}C	τ_0, Pa at 20 ^{0}C	C_P, %	C_R, %	C_A, %
1	810,4	12	4,4	0,03	0	13,3	6,8	0,2
2	829,7	21	4,9	0,16	0	15,4	7,9	0,6
3	848,5	27	29,0	39,27	2,42	22,6	15,2	2,3

The chromatographic analysis shows that the oils contain n-alkanes of C_{15} - C_{44} group. The content of C_{15} - C_{19} paraffin is 5.1% - 7.7%, C_{20} - C_{29} paraffin is 7.4% - 11.1% and C_{30} - C_{44} paraffin is 0.9% - 3.8% respectively. The nucleation temperature (NT), crystal formation temperature (CFT) and paraffin melting temperature (PMT) of oils were determined by differential scanning calorimetry (DSC) and microscopy[13].

The DSC data of Uzen oil in the course of heating and cooling processes are presented in Figure 1. During the heating of cooled oil sample two peaks appear: exothermic peak with maximum at 27.1 °C and endothermic peak at 56.5 °C. The exothermic peak is probably responsible for release of liquid phase from the ODS, for example, corresponds to transition of ODS from the bounded-dispersal to free-dispersal state because its temperature coincides well with PP of oil (Table 1). The endothermic peak is related to PMT and correspondingly to transfer of ODS into molecular – dispersed state. In cooling curve the exothermic peak with maximum at 48.4 °C corresponds to wax appearance temperature (WAT)[14]. Below 35 °C the decaying part of endothermic peak is related to immobilization of liquid medium.

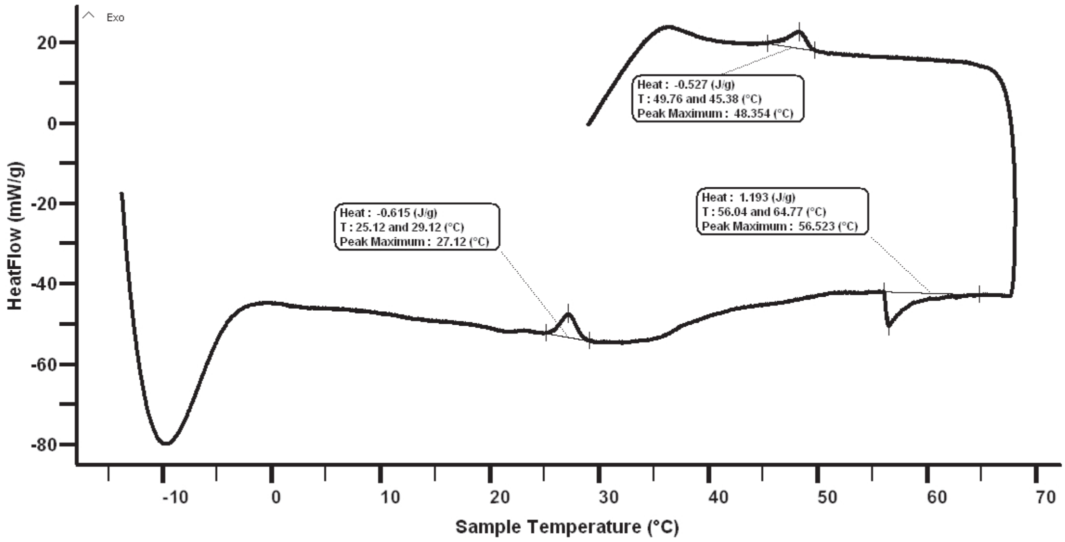

Figure 1
DSC Curve of Uzen Oil (Heating-Lower Curve, Cooling-Upper Curve) (Mass of the sample is 0.2 g)

Microscopic and DSC data characterizing the change of ODS state are summarized in Table 2. Comparison of these results with the data of Tables 1 shows, that interrelationship between the values of oil composition, NT, CFT and WAT is in good correlation-the higher mass fraction of paraffin, especially high-molecular-weight paraffin, the higher values of NT, CFT and WAT. The enthalpy of transition from the free-dispersal to bounded-dispersal states and back increases with increase of paraffin content in oil.

Table 2
Data of Microscopy and DSC for Kumkol (1), Akshabulak (2) and Uzen Oils (3)

Number #	PLM		DSC					
	NT, °C	WAT, °C	WFT, °C	ΔH, J·g^{-1}	WAT, °C	ΔH, J·g^{-1}	PP, °C	ΔH, J·g^{-1}
1	52	40 - 45	49.5 - 52.2	0.248	38.9 - 42.3	-0.239	10.9 - 13.9	-0.375
2	56	45 - 50	-	-	-	-		
3	67	50 - 55	56.0 - 64.7	1.193	45.4 - 49.8	-0.527	25.1 - 29.1	-0.615

Due to decreasing of paraffin content the values of kinematic viscosity, shearing stress and dynamic shearing yield stress decrease in the following order: Uzen > Akshabulak > Kumkol. The Kumkol and Akshabulak oils exhibit Newtonian behavior between temperatures 20 - 50 °C in spite of existing in free dispersed state. Deviation from the Newtonian behavior is observed for Uzen oil at temperature below 40 °C.

Rheological data, the values of NT, WAT and PP for thermally untreated Kumkol, Akshabulak and Uzen oils show that the free dispersed state is realized between temperatures 9 - 50 °C, 18 - 56 °C and 24 - 65 °C. These parameters are defined by oil composition and molecular mass distribution (MMD) of paraffins.

2.2 The Influence of Heat Treatment on the Behavior of ODS

The total melting of solid paraffin provides transition of ODS to molecularly-dispersed state. For precise determination of low temperature limit of molecularly-dispersed state the Uzen oil was thermally treated at temperature interval between 60 - 90 °C with heating rate of 10 °C during 30 min. Rheological parameters of oils before and after heat treatment (HT) are summarized in Table 3.

As follows from the Table 3, the minimum values of PP and rheological parameters for Kumkol and Akshabulak oils are observed after HT at 70 ^{0}C, and for oil of Uzen, which is at 90 ^{0}C that points to transition of systems to a molecular-disperse state.

Table 3
Change of Rheological Parameters of Kumkol (1-4), Akshabulak (5-8) and Uzen (9-12) Oils in Dependence of Heat Treatment Temperature (HTT)

Number #	HTT, °C	T, °C for η and τ_0	η, Pa•s (D = 5c^{-1})	τ_0, Pa	PP, °C
1	50	5	1.973	3.819	12
2	60	5	0.324	0.165	6
3	70	5	0.036	0.045	0
4	80	5	0.030	0	0
5	50	5	0.962	3.430	15
6	60	5	0.434	1.131	9
7	70	5	0.078	0.012	3
8	80	5	0.028	0	3
9	60	25	6.352	16.274	27
10	70	25	2.085	0.621	24
11	80	25	0.321	0.024	21
12	90	25	0.175	0	18

The identified temperature impact on ODS is confirmed by results of paraffin crystals' morphology which were obtained for non-processed and thermally treated oil samples. The results of polarizing microscopy show that paraffin in crude oils is mainly in a type of small star-shaped crystals with an average size from 2 to 10 μm. Increasing the number and aggregation of such crystals with decreasing of temperature leads to formation of three-dimensional network preserving the dispersive environment of oil[2, 15].

Due to this fact it is specific for crude oil the high values of shearing stress, apparent viscosity and PP.

HT leads to generation of larger and densely paraffin associates with laminar poligonal shape. The reason is that asphaltenes and resins containing in oil play the role of natural surfactants and cause suppressive action on growing of paraffin monocrystals. Therefore the formation of strong spatial paraffin structure in thermally treated oil takes place at lower temperature in comparison with crude oil[2,16].

Rheological behavior of oil depends not only on HTT but also is the function of cooling rate. According to[13] the largest paraffin-resin conglomerates generated at optimal cooling rate are non-uniformly distributed within the whole volume and decrease the rheological characteristics of oil.

Influence of cooling rate to morphology of paraffin crystals was studied for Uzen oil sample. After HT of oil at 90 °C the oil was cooled at the rate of 5, 10, 15, 20, 25, 30, 40 °C•hour^{-1}. Shearing stress of Uzen oil has the highest value at cooling rate 5 and 10 °C•hour^{-1} (Figure 2). Increasing of the cooling rate leads to improving of rheological behavior of oil, the minimal values of shearing stress are observed at 20 °C•hour^{-1}. The further increasing of cooling rate results in worsening of oil fluidity. Rheoviscometric data are in good agreement with results of Uzen oil's paraffin crystals morphology cooled at different rate. It follows from the microphotography analysis that the structure, at which the liquid phase of oil is preserved in smallest degree, is observed for oil cooled at the rate of 20 °C•hour^{-1}. Extreme dependence of the rheological characteristics and size of paraffin crystals on cooling rate of ODS, is due to existing of optimal ratio of nucleation rate and crystal growth, which provides forming of the most mobile ODS structure.

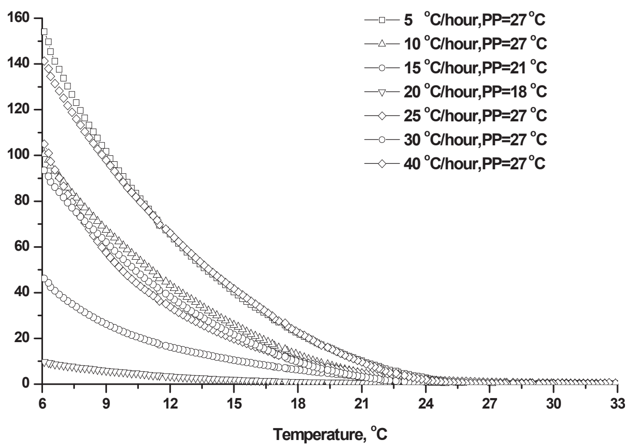

Figure 2
Influence of Uzen Oil Cooling Speed to Temperature Dependency of Shearing Stress, Shearing Speed is 5 s^{-1} (HT at 90 °C)

Thus the heat treatment allows to expand the temperature zone of free dispersal state of paraffin oils up to 9-18 ^{0}C, while the width of the zone depends on oil composition, HTT and cooling rate. The maximal temperature interval of freely-dispersed state of paraffin oil obtained in the course of HT is -3 - 52 ^{0}**C**, 0 - 56 ^{0}**C**, 15 - 65 ^{0}**C** for Kumkol, Akshabulak and Uzen oils respectively.

2.3 Study of the ARPD Formation of High Paraffin Oils on the Steel Surface

Studying of ARPD formation of Kumkol, Akshabulak and Uzen oils on the steel surface was carried out by methods of chromatography, microscopy and chemical analysis using “cold finger” apparatus.

The results are presented in Table 4. As seen from Table 4 the increase of temperature gradient between oil and steel surface leads to decrease of mass, increase of hardness and changing of ARPD composition.

Analysis of ARPD sample shows that it is heterogeneous by consistency and consists of solid and loose components. The solid part strongly adhered to cold finger differs by absence of mechanical admixtures and low content of asphaltenes and resins. Paraffin content in solid part of ARPD is lower in comparison with loose part. However, the solid part contains larger number of long-chain paraffin C_{30}-C_{48}. These paraffin sediment firstly on the surface of cold finger, forming solid and hardly removable layer. While the loose part of ARPD contains the higher content of mechanical additives, asphaltene-resin substances and prevailing amount of long-chains paraffin (C_{21}-C_{29}). The loose part of ARPD forms the external layer of sediments and due to such features of component structure, can easily be removed and dissolved in oil.

Table 4
Characteristics of the ARPD Isolated From Kumkol (1-4), Akshabulak (5-9) and Uzen (10, 11) Oils Without HT

Number #	T_{oil}, ^{0}C	ΔT, ^{0}C	Mass of ARPD, g	C_{oil}, %	C_{W+MA}, %	C_{R+A}, %	C_P, %	C_{20}-C_{29}, %	C_{30}-C_{44}, %
1*	50	44	4.8	0	0	43.8	54.9	22.5	29.9
2*	40	34	7.8	1.2	1.5	46.5	49.7	21.2	26.0
3**	30	24	7.2	4.4	2.1	51.2	42.1	20.0	19.4
4**	20	14	7.8	10	3	58.2	28.6	17.6	9.7
5*	60	48	6.6	0	0	39.7	58.8	32.7	25.5
6*	50	38	7.2	0	0	44.5	53.2	30.0	22.7
7*	40	28	15	0	1.3	46.7	50.4	30.9	18.1
8**	30	18	18.4	6.2	3.8	48.2	39.9	28.3	10.2
9**	20	8	20.2	12.6	4.7	45.5	36.8	29.7	6.0
10*	50	40	20	0	0	33.2	65.5	34.3	29.0
11**	40	30	32	5.8	3	37.8	52.9	37.1	6.8

* firm, strong samples of deposits with high adhesion to a steel surface,
** friable, fragile samples of deposits with low adhesion to a steel surface.

These data are in good agreement with DSC results of Uzen oil ARPD. The maximum values of WAT for samples of ARPD from Uzen oil isolated at temperatures of oil of 40, 50 and 60 ^{0}C ($T_{\text{cold core}}$ = 10 ^{0}C) are equal to 50.7; 53.8 and 60.3 °C. The enthalpy of paraffin crystals formation from ARPD at 50 and 60 °C (-1,205 and -1,213 $J \cdot g^{-1}$) is two times higher than that at 40 °C (-0.64 $J \cdot g^{-1}$). In the latter case the crystallization of short-chain paraffins (C_{21}-C_{29}) takes place.

Thus contacting of high paraffinic oil with steel surface leads to deposition of ARPD. Its content, composition and adhesive ability depends on oil composition and gradient of temperature between oil and metallic surface (Δ*T*). At Δ*T* > 30 °C the solid and crystalline ARPD enriched by long-chain high-melting paraffins with high adhesion to metallic surface is formed. At Δ*T* < 20 °C loose, weak, easily removable ARPD that enriched by mechanical admixtures, water, resin, asphaltene and short-chain low-melt paraffins.

CONCLUSIONS

Composition, rheological parameters, the values of NT, WAT, WDT and PP of Kumkol, Akshabulak and Uzen crude oils were determined. It was established that the rheological parameters and phase transition temperatures of ODS are determined by oil composition and MMD of paraffins. The free–dispersal state of ODS can be realized at temperature interval between 9 - 52 ^{0}C, 18 - 56 ^{0}C, 24 - 65 ^{0}C for Kumkol, Akshabulak and Uzen oil respectively.

Heat treatment expands the temperature zone of free-dispersal state of paraffin oils (zone of the ODS stability) due to decreasing of PP. Depression of PP is defined by oil composition, HTT and rate of cooling. Maximal value of PP depression after HT is 12 ^{0}C, 15 ^{0}C, 9 ^{0}C for Kumkol, Akshabulak and Uzen oils respectively.

Contacting of ODS with steel surface leads to APRD formation. Its quantity, composition, structure and adhesive ability depends on oil composition and temperature gradient between oil and steel surface. At $\Delta T > 30$ °C the solid and crystalline ARPD enriched by long-chain high-melting paraffins with high adhesion to metallic surface is formed while at $\Delta T < 20$ °C the formation of loose, weak, easy removable ARPD enriched by mechanical admixtures, water, resin, asphaltene and short-chain low-melt paraffins is observed.

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