Study on The Effect of Demulsifers on Crude oil and Petroleum Products

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ABSTRACT: The oil refining industries are using a number of demulsifiers for dewatering and desalination of crude oil but experience has shown that universal demulsifiers can not be produced. Each kind of water in oil (W/O) emulsion requires specific by composition demulsifier. In practice, synergetic effect of the interaction between different types of demulsifiers is often sought. For dewatering the water in oil emulsion of crude oil from the Ural region, 16 kinds of demulsifiers were tested, named D1 ÷ D16. With combinations of demulsifiers, the highest rate of emulsion drying was observed with mixture 1 (2.5 ppm of demulsifier D5 and 2.5 ppm of demulsifier D9). For the emulsion of water with diesel fraction boiling in the temperature range 180-360°C, mixture 1 at concentration of 20 ppm gave the optimal effect in breaking the emulsion. The results obtained from the experiments showed that the overdosing of demulsifier did not lead to optimal emulsion breaking and laboratory and industrial scale experiments should be carried out to break specific emulsion.

Key words: Water in oil emulsion (W/O), Solubility in water, Rate of destruction, Diesel distillates, Synergetic effect

INTRODUCTION

Crude oil, except petroleum gas, is the fuel with the highest calorific value of 44÷48 MJ/kg and it has solved a number of energy problems of mankind. However, freshly extracted oil includes water from different levels containing chlorides, sulfates, nitrates, and other inorganic compounds. The water forms stable water-oil emulsions which increase transportation costs and impede its preparation for processing. The water and the chlorides dissolved in it are unwanted impurities with strong corrosion effect on the technological equipment. They also deteriorate the quality of petroleum distillates, especially fractions of heavy components such as boiler fuel, raw material for catalytic cracking and others. Both at the oil fields and oil refineries, a number of methods are used to remove water, chlorides and other impurities from oil. In recent years, water-oil emulsions were successfully separated on the basis of relationships defined in modern physical chemistry of emulsions and surface phenomena. The methods invented allow for quick stratification of water by surface-active agents (surfactants), called demulsifiers. In emulsions the forces of intermolecular interaction are acting and there is surface tension at the phase boundaries. Due to surface tension, all liquids are tending to reduce their surface area to

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minimum. Furthermore, the individual drops tend to coagulate into larger ones. The emulsion of pure water and pure oil is unsustainable. The dispersed phase coagulates to form two separate layers (Frolov, 1995; Shchukin, 2006; Shchukin *et al.* 2006). The repulsion forces between the water and oil molecules can be reduced which would give reduced surface tension between the two phases. It is achieved by a introducing a third component in the system called emulsifier or stabilizer. The emulsifier is adsorbed between the phases and decreases the surface tension to form a strong adsorption layer around the particles of the dispersed phase (Shchukin, 1999). Such stabilization is principally possible when the substances used, due to their structure, can interact with the molecules of both water and oil. The stability of the oil emulsions is affected also by their dispersity. Emulsions of higher dispersity are more stable (Shchukin *et al.,* 2001). The increase of temperature leads to decreases oil density and viscosity, as well as emulsion stability. The drop size of the dispersed phase also affects the emulsion stability. According to the water droplets sizes, emulsions are classified as: less than 20 μm – micro dispersed emulsions, from 20÷50 μm - average dispersed emulsions, and more than 50 μm – coarsely dispersed emulsions. The micro

dispersed emulsions are most difficult to destroy. Life time of the emulsion also affects its stability. Emulsions, particularly of the type W/O, become more stable with time. The phenomenon is called aging of emulsions. It is much harder to destroy old oil emulsions because the thickness of the protective layer formed at the interphase boundary increases and enhances the stability of the emulsion. The content of emulsifiers, chlorides, solvents also affects the emulsion stability.The electrolytes, such as $MgCl_2$, $CaCl_2$, NaCl, solved in water droplets help the transition of the emulsifiers in gel-like state and thereby facilitate the destruction of the emulsion. Solvents like benzene and toluene also facilitate the destruction of emulsions (Fingas, 1995; Fink, 2003; Fingas and Fieldhous, 2003). The oil refining industries are using a number of demulsifiers for dewatering and desalination of crude oil but experience has shown that there are no universal demulsifiers. Depending on emulsion type, it is necessary to select the proper demulsifier or its composition. The common practical approach is to use the synergetic effect and interaction between several demulsifiers. There are various methods for assessing the effectiveness of crude oil demulsifiers. There are methods for determining demulsifier effectiveness, based on a modification of the electrical conductivity of water/oil emulsions (Messenger, 1999; Ye *et al.*, 2009). Another method is based on the determination of the structure and mechanical properties of the boundary layers of water-oil emulsions (Dalmazzone *et al.*, 2005; Dicharry *et al.*, 2006; Daniel-David *et al.*, 2008; Quintero *et al.*, 2008). However, the most popular are the methods based on "Bottle test" (Noik *et al.*, 2003; Poindexter *et al.*, 2003). The data obtained by this method characterize a demulsifier at certain temperature and concentration. During the test, the quality of the separated water is also estimated (e.g. clear, cloudy, containing oil). The objectives of this work are:
- To explore the possibility of destruction of the water-oil emulsion of Urals crude oil by demulsifiers;
- To find the optimal demulsifier or a combination of them for dewatering crude oil from Ural origin;
- To examine the possibility of destruction of water emulsions of diesel oil distillates.

MATERIALS & METHODS

Petroleum refineries have units for primary preparation of oil using a combination of electrochemical and thermal methods of dehydration and desalting. In recent years, significant results were obtained as a result of process optimizations like implementation of effective demulsifiers, modern structures of electrical devices, new mixing devices for regulating the amount of water-oil emulsions and

others. Depending on the crude oil origin, the content of chlorides at the entrance of distillation plants ranges from 5 to 280 mg/dm^3 and the water content of 0 to 3% v/v. In the process of preparation, the oil chlorides content in it should be reduced below 5 mg/dm^3, and the water content – below 0.1% v/v. For complete desalination of oil, washing with water is used. The water reverses the phases in the emulsion and dissolves the chlorides from crude oil and other unwanted impurities. For the purposes of this study, crude oil Ural type was used and its properties are shown in Table 1.

Table 1. Physicochemical properties of the oil

Properties	Value
1. Density 15°C, g/cm^3	0.8770 ± 0.0004
2. Molecular weight, g/mol	237 ± 5
3. Viscosity, cSt	
20°C	17.21 ± 0.18
30°C	12.50 ± 0.12
40°C	9.18 ± 0.08
50°C	6.98 ± 0.04
4. Parrafin content, %	6.2 ± 0.6
5. Pour point, °C	$(-8) \pm 2$
6. Viscosity index	
20°C	2.62 ± 0.5
30°C	2.10 ± 0.5
40°C	1.78 ± 0.5
50°C	1.57 ± 0.5
7. Elemental composition, %	
S	1.72 ± 0.05
C	85.23 ± 1.20
H	12.65 ± 0.12
N	0.15 ± 0.01
O	0.25 ± 0.02
8. Water, %	0.10 ± 0.02
9. Salts, mg/dm^3	41.0 ± 2.5
10. Sediments, %	0.016 ± 0.004
11. Distillation, %v/v	
IBP, °C	54 ± 1
Up 62°C	1.0 ± 0.2
Up 85°C	2.0 ± 0.3
Up 120°C	7.0 ± 0.4
Up 150°C	12.0 ± 0.8
Up 180°C	17.0 ± 1.0
Up 200°C	20.0 ± 1.0
Up 240°C	28.0 ± 1.0
Up 250°C	30.0 ± 1.0
Up 300°C	39.0 ± 1.0
Up 350°C	52.0 ± 1.0
12. Asphaltenes, %	6.6 ± 0.8

Taking into account that all the companies producing demulsifiers are trying to develop as universal as possible and effective demulsifiers for oil dewatering, we used samples produced by four companies in our experiments. For dewatering of water-oil emulsion from Ural crude oil, sixteen samples were tested, named: D1 ÷ D16 (Table 2). The experiments were carried out by a technique based on the principle of the method of "test in a bottle". The essence of the methodology is as follows: a sample of 5 l of Ural crude oil was taken for the determination.

The oil was divided into 93 cm^3 portions and placed in beakers of 250 cm^3. The samples were heated to 60°C under continuous stirring with a mixer at 1500 min^{-1}. Then, 20 ppm of demulsifier and 7 cm^3 of water are added (93:7 – was the minimum quantity of water for best separation of the emulsion type W/O). The resulting emulsion is transferred into graduated cylinders, which are placed in a water bath at 90°C. Then the quantity of water separated after 5, 10, 20, 30, 60, 120 and 180 min is measured in cm^3, thus recording the emulsion breaking speed, respectively the demulsifier activity.

RESULTS & DISCUSSION

The data in table 1 show that the Ural crude oil can be characterized as average sulfur content type. However, typical for this material is that it contains higher boiling petroleum fractions. These qualities classify the crude oil studied into the group of oils for which the water-oil emulsions are quite difficult to break. As a result of the experiments carried out with

commercial products according to the method described above, it was found that among the products D1 ÷ D4, demulsifier D1 had the highest rate of dehydration (Fig. 1).

The higher activity of sample D5 was proved by the results in Fig. 2.

The results in Fig. 3 show that the demulsifier D9 had the highest effectiveness.
Samples D13, D14, D15 and D16 (Fig. 4) can be arranged by their activities in the following order:

D13 > D14 > D15 > D16

Therefore, demulsifier D13 can successfully be used to dry Ural crude oil.

Analyzing the results presented in Fig. 1÷ 4, the activities of demulsifiers D5, D9, D13 and D1 were compared (Fig. 5). The demulsifier D5 was found to have the highest rate of destruction of water-oil emulsion.

It is known from practice (Bhardwaj and Hartland, 1993; Bhardwaj and Hartland, 1994; Kim *et al.*, 1995) that demulsifiers' activity depends on their dosage, so varying concentrations of demulsifier D5 ranging from 1 to 15 ppm were tested in experiments on crude oil dehydration.It can be seen from the results shown in Fig. 6 that the optimal concentration of demulsifier D5 for dehydration of Ural oil is 5 ppm.

The effect of combinations of demulsifiers on the destruction of water-oil emulsion was also studied with the following mixtures (Fig. 7):

Table 2. Typical properties of demulsifiers

| Demulsifier	Viscosity at 20°C	Flash Point	Density at 20°C	Solubility in Water
	(cSt)	(°C)	(g/ml)	
D1	430 ± 20	115 ± 3	1.030 ± 0.001	Insoluble
D2	2000 ± 80	135 ± 3	1.030 ± 0.001	Insoluble
D3	720 ± 30	99 ± 3	1.050 ± 0.001	Insoluble
D4	1700 ± 60	89 ± 3	1.040 ± 0.001	Insoluble
D5	90 ± 8	81 ± 3	0.970 ± 0.001	Dispersible
D6	55 ± 5	81 ± 3	0.970 ± 0.001	Dispersible
D7	1700 ± 65	135 ± 3	1.062 ± 0.001	Insoluble
D8	430 ± 20	81 ± 3	1.009 ± 0.001	Insoluble
D9	1850 ± 70	98 ± 3	1.059 ± 0.001	Insoluble
D10	470 ± 25	63 ± 2	0.999 ± 0.001	Insoluble
D11	130 ± 15	78 ± 3	1.000 ± 0.001	Insoluble
D12	150 ± 18	80 ± 3	0.962 ± 0.001	Insoluble
D13	200 ± 25	121 ± 3	1.049 ± 0.001	Soluble
D14	2400 ± 100	98 ± 3	1.020 ± 0.001	Insoluble
D15	170 ± 10	31 ± 2	0.932 ± 0.001	Dispersible
D16	300 ± 35	121 ± 3	1.074 ± 0.001	Soluble
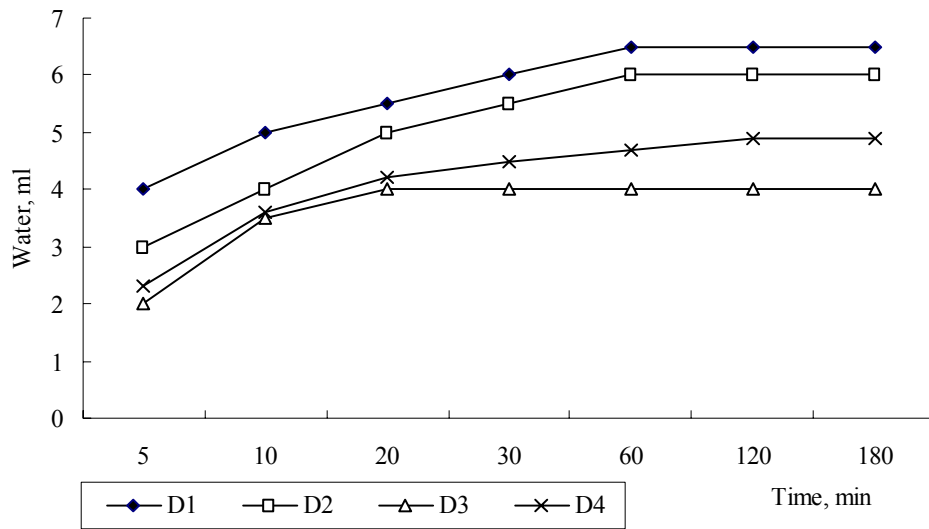
Fig. 1. Rate of destruction of W/O emulsion with demulsifiers D1, D2, D3 and D4
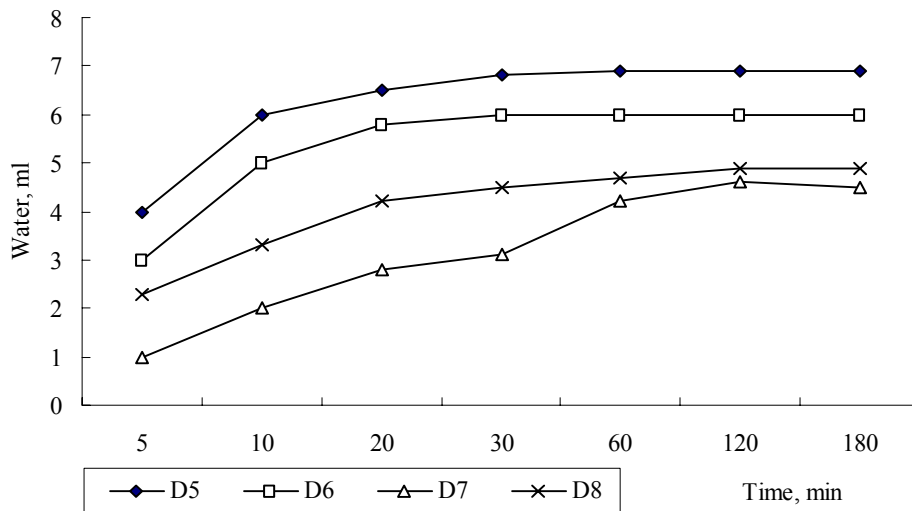

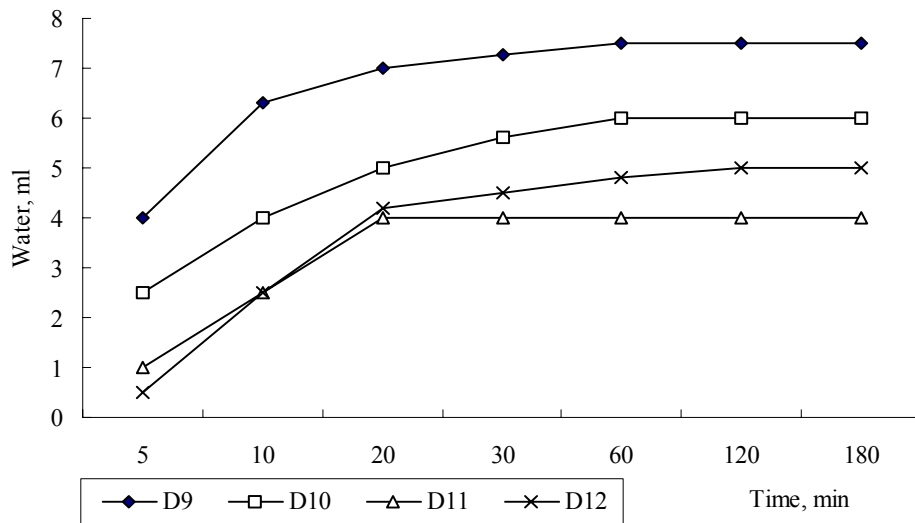**Fig. 2. Rate of destruction of W/O emulsion with demulsifiers D5, D6, D7 and D8**

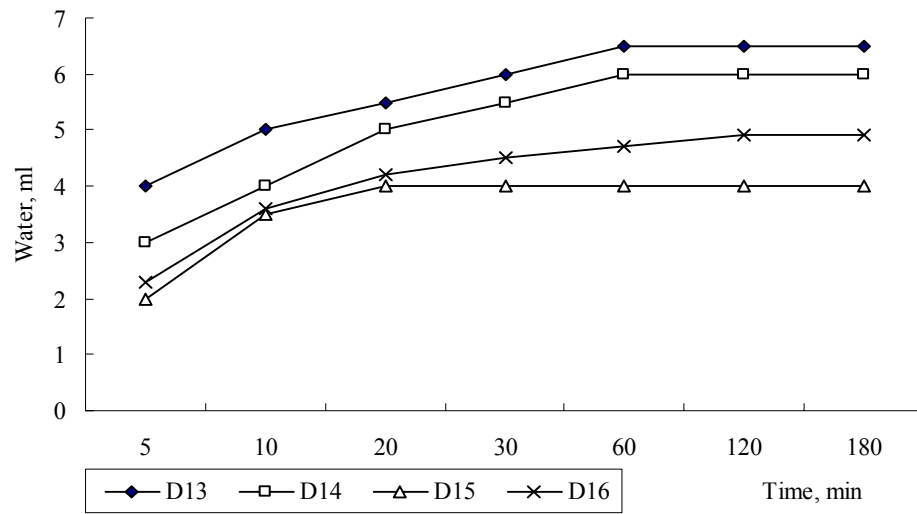**Fig. 3. Rate of destruction of W/O emulsion with demulsifiers D9, D10, D11 and D12**

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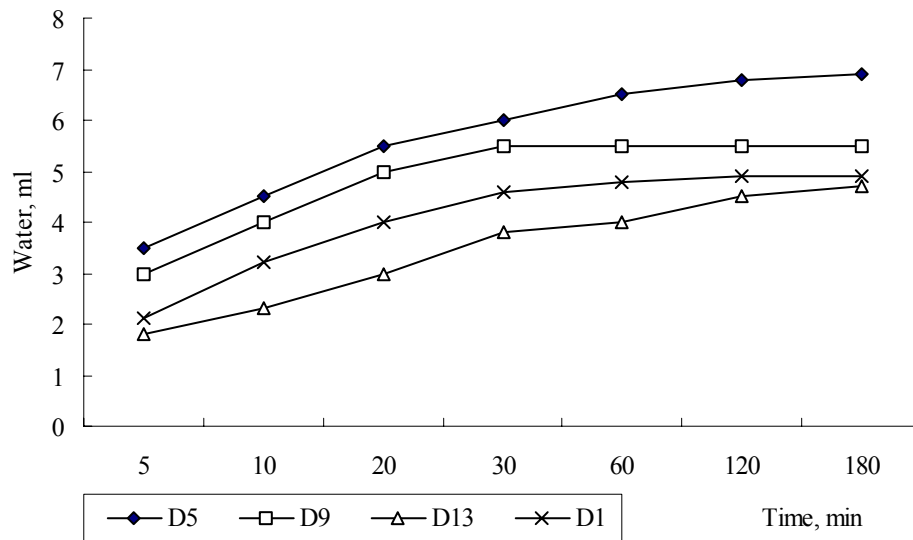**Fig. 4. Rate of destruction of W/O emulsion with demulsifiers D13, D14, D15 and D16**

Fig. 5. Rate of destruction of W/O emulsion with demulsifiers D5, D9, D13 and D1
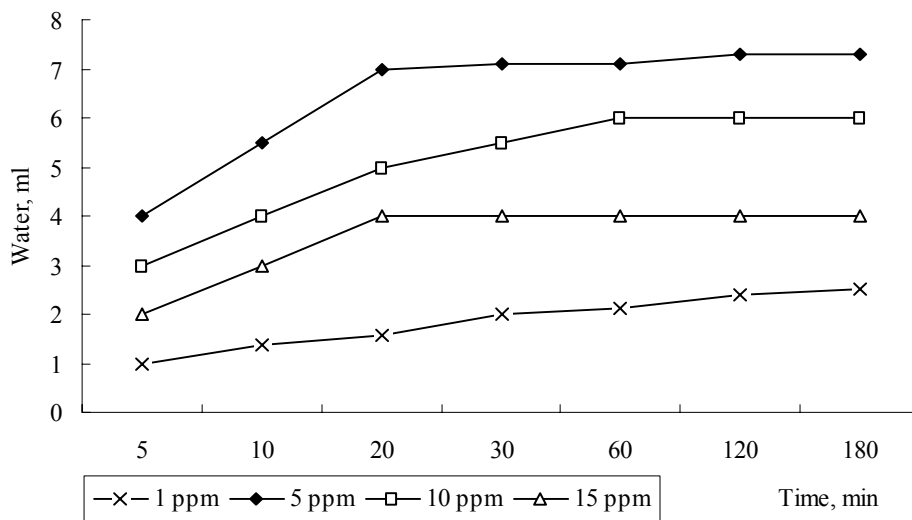

Fig. 6. Rate of destruction of W/O emulsion with demulsifier D5

- Mixture 1) 2.5 ppm of demulsifier D5 and 2.5 ppm of demulsifier D9;
- Mixture 2) 2.5 ppm of demulsifier D5 and 2.5 ppm of demulsifier D13;
- Mixture 3) 2.5 ppm of demulsifier D5 and 2.5 ppm of D1.

It can be concluded from the results obtained with mixtures of demulsifiers that mixture 1 had the highest rate of drying of the emulsion. Comparing the activities of demulsifier D5 and mixture 1 at the same concentration (Fig. 7), mixture 1 obviously had higher activity than demulsifier D5 which is a sound confirmation of the rule for selecting demulsifiers, namely: "A specific composition for certain type of crude oil". For the purposes of the study, a large diesel fraction of Ural crude oil boiling in the range 180÷360°C

was separated. The main characteristics of the fraction are listed in Table 3.

With this fraction, water emulsion was prepared at temperature of 20°C and homogenization time of 30 min. The emulsion was treated with a mixture of reagents (mixture 1) in accordance with Fig. 7. The results of the experiments are shown in Fig. 8 and they indicate that the optimal effect in breaking the emulsion was achieved with mixture 1 at a concentration of 20 ppm.

The results obtained during the present study showed that excessive overdosing of demulsifiers up to 50 ppm did not lead to optimal destruction of the emulsion and specific laboratory and industrial experiments have to be carried out with every emulsion to select the best reagent and its optimal concentration.
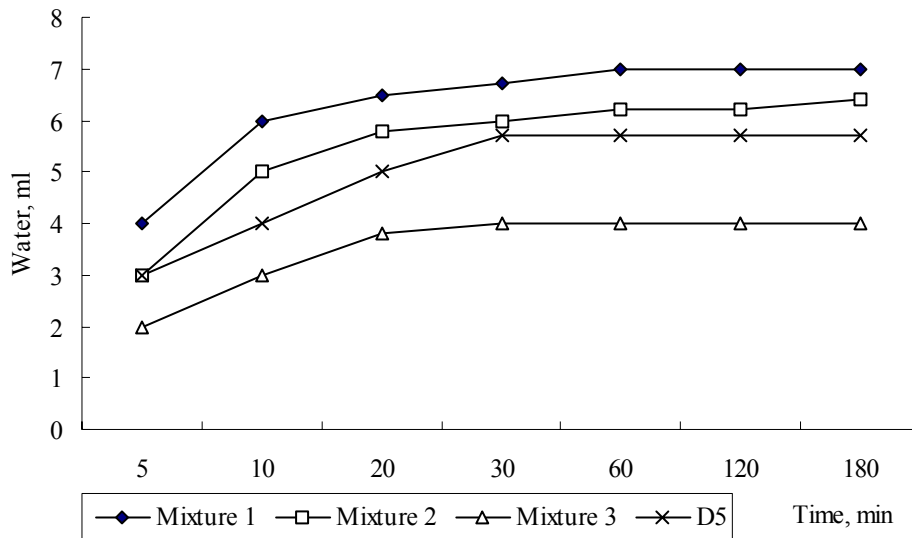

Fig. 7. Rate of destruction of W/O emulsion with mixtures 1, 2 and 3

Table 3. Main characteristics of the fraction 180 ÷ 360°C

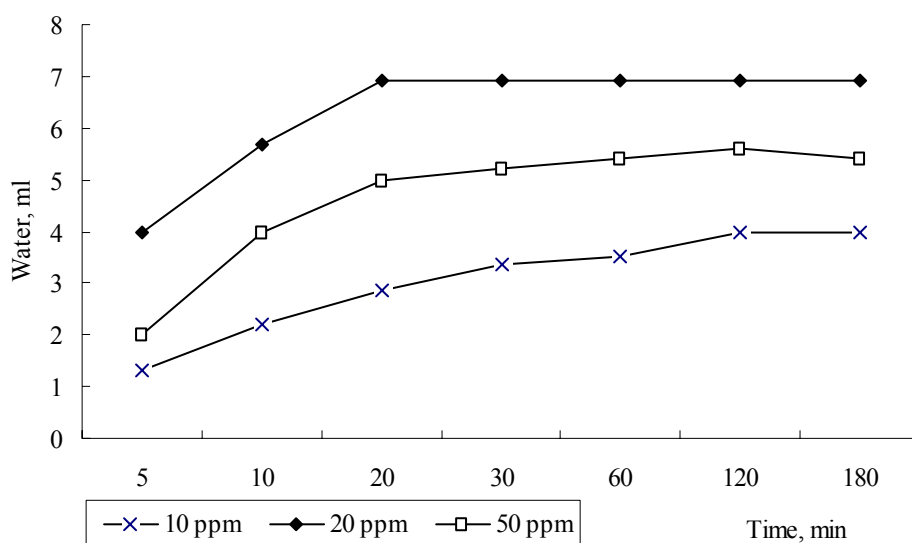| Properties	Fraction 180÷360°C
	180÷360°C
1. Density at 15°C, g/cm^3	0.8469
2. Kinematic viscosity	
3. Sulfur, mg/кg	356
4. Water, mg/кg	84
5. Distillation characteristics	
- IBP, °C	182
- up 250°C, %v/v	41
- up 350°C, %v/v	93
- 95 %, °C	355
- FBP, °C	361

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Fig. 8. Rate of destruction of W/O emulsion by fraction 180÷ 360°C

CONCLUSION

Sixteen demulsifiers for dehydrating of water-oil emulsion from Urals crude oil, named: D1 ÷ D16 were tested. The highest rates of crude oil drying were observed with demulsifiers D1, D5, D9 and D13. The demulsifier D5 showed the highest rate of destruction of the water-oil emulsion. It was found that the optimal concentration of the demulsifier D5 for dehydrating of Urals crude oil is 5 ppm. With combinations of demulsifiers, the highest rate of emulsion drying was observed with mixture 1 (2.5 ppm of demulsifier D5 and 2.5 ppm of demulsifier D9). For the emulsion of water with diesel fraction boiling in the temperature range 180-360°C, mixture 1 at concentration of 20 ppm gave the optimal effect in breaking the emulsion. The results obtained in the study showed that excessive overdose of demulsifiers up to 50 ppm, did not lead to optimal destruction of the emulsion and specific laboratory and industrial experiments have to be carried out with every emulsion to select the best reagent and its optimal concentration.

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