Investigation of the Surface Tension Coefficient of the Depressant Additive and Components of Oil

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Abstract

For the first time in laboratory conditions, the coefficient of surface tension of the depressant additive "Difron-4201" and polar-molecular asphaltene-resinous components of highly paraffinic model oil were determined. During the experiment, a solution of depressant additive and asphaltene-resinous components in toluene was used. The concentration of the solution was increased to a constant value of the surface tension coefficient was established, and water was used as the standard liquid. The ring detachment method (du Noüy) was used to determine the tension coefficient of the surface of the depressant additive and asphaltene-resinous heterocomponents, and the measurement process was carried out on a tensiometer with a relative error of ± 1%. The results of the experiments showed that the surface tension coefficient increases with an increase in the concentration of the additive, asphaltene-resinous components in the solution. Analysis of the values obtained during the measurements showed that the surface tension coefficient of the asphaltene components of the highly paraffinic model oil is higher than the surface tension coefficient of the depressant additive Difron-4201, and the surface tension coefficient of the resin components is close to the value obtained in the additive. This result gives reason to believe that it is the resin components that affect the effectiveness of the depressant additive.

Keywords: surface tension coefficient, highly paraffinic model oil, depressant additive "Difron-4201", asphaltene-resinous components, surface-active substance (SAS), viscosity, temperature.

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Depressor aşqarın və neft komponentlərinin səthi gərilmə əmsalının tədqiqi

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Annotasiya

İlk dəfə olaraq laboratoriya şəraitində “Difron-4201” depressor aşqarının və yüksəkparafinli model neftin polyar molekullu asfalten-qətran komponentlərinin səthi gərilmə əmsalı təyin edilmişdir. Təcrübədən alınan nəticələrdən məlum olmuşdur ki aşqarın, asfalten və qətranın məhlulda qatılığı artdıqca səthi gərilmə əmsalı da artır. Ölçmələr zamanı alınmış qiymətlərin analizi yuksək parafinli model neftinin asfalten komponentlərinin səthi gərilmə əmsalının qiymətinin “Difron-4201” depressor aşqarının səthi gərilmə əmsalının qiymətindən yüksək, qətran komponentlərinin səthi gərilmə əmsalının qiymətinin isə aşqarda alınan qiymətə yaxın olduğunu göstərmişdir. Belə bir nəticə “Difron-4201” depressor aşqarının effektliyinə məhz qətran komponentlərinin təsir etdiyini deməyə əsas vermiş olur.

Açar sözlər: səthi gərilmə əmsalı, yüksək parafinli model neft, “Difron-4201” depressor aşqarı, asfalten-qətran komponentləri, səthi aktiv maddə.

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Исследование коэффициента поверхностного напряжения депрессорной присадки и компонентов нефти

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Аннотация

Впервые в лабораторных условиях определен коэффициент поверхностного натяжения депрессорной присадки «Дифрон-4201» и полярно-молекулярных асфальтеносмолистых компонентов высокопарафиновой модельной нефти. Результаты экспериментов показали, что коэффициент поверхностного натяжения увеличивается с увеличением концентрации добавки, асфальтеносмолистого компонента в растворе. Анализ значений, полученных в ходе измерений, показал, что коэффициент поверхностного натяжения асфальтеновых компонентов высокопарафинового модельного нефти выше, чем коэффициент поверхностного натяжения депрессорной присадки «Дифрон-4201», а коэффициент поверхностного натяжения компонентов смолы близок к значению, коэффициент поверхностного натяжения депрессорной присадки «Дифрон-4201». Этот результат дает основание полагать, что именно смоляные компоненты влияют на эффективность депрессорной добавки.

Ключевые слова: коэффициент поверхностного натяжения, высокопарафиновое модельное нефть, депрессорная присадка «Дифрон-4201», асфальтеносмолистые компоненты, поверхностно-активное вещество (ПАВ), вязкость, температура.

Introduction

Undoubtedly, in the next new decade, the oil and gas sector will continue to be a priority component of the global energy base.

The main tasks in the development of this sector in modern times are the development of energy-saving technologies and increasing the efficiency of existing main oil pipelines.

One of the ways to solve this problem is the use of chemicals that improve the rheological properties of oils and petroleum products, provide complete cleaning of the pipe cavities, and significantly reduce the energy consumption for transmission.

With the development of the chemical industry, the range of reagents expands, and, accordingly, the scope of their application grows. In this case, narrower specialized reagents are created to solve specific problems in the transportation of oil through pipelines. Thus, the use of chemical reagents is becoming one of the most promising ways to improve pipeline transport and the operation of oil pipelines.

It is known that oils with high paraffin content include oils with a paraffin content of more than 6% by weight of oil. Oils with a high paraffin content exhibit special non-Newtonian properties, expressed in the presence of maximum static shear stress and the dependence of the viscosity on the velocity gradient at transfer temperatures in a conventional pipeline.

At low temperatures, such oils can lose mobility, making it difficult to transport them through pipelines. When transporting highly paraffinic oil through pipelines, various methods are used to increase their fluidity, in particular, the addition of depressants.

Pipeline transportation of high-paraffinic oils with the addition of depressants are considered one of the most promising methods of transporting high-paraffin oil.

The use of depressant additives makes it possible to significantly reduce hydraulic losses during transportation of high-paraffin oils, reduce the amount of asphalt-resin-paraffin deposits on the walls of pipelines and equipment, as well as facilitate the operation of oil field and oil pipeline equipment [1-6].

Surface phenomena play an important role in the fight against asphalt-resin-paraffin deposits in the oilfield equipment, as well as in the processes of oil production, treatment, transportation and refining.

Although additives are widely used to prevent the formation of wax deposits, there is still no unified theory to explain their mechanism of action. Therefore, the selection of depressants for dispersed oil systems is carried out only empirically.

It is known that all additives have the properties of surfactants (surfactants). Therefore, in addition to the mechanism of their volumetric action, there is information in the literature on the surface mechanism. The effectiveness of the effect of depressants is inversely proportional to their surface tension coefficient of [7-9].

The effectiveness of most additives is also affected by polar molecular asphaltenes and resin components of dispersed petroleum systems. This is most likely due to their surface-active properties. For this reason, the study of the surface tension coefficient of the used depressants and asphaltene-resinous components of highly paraffinic oils is of scientific and practical importance.

The purpose of the work

Determination of the coefficient of the surface tension of the depressant additive "Difron-4201" and polar molecular asphaltene-resinous components of high-paraffinic model oil in laboratory conditions.

Experience methodology

During the experiment, were used asphaltene-resinous components of the model oil sample with physicochemical characterristics given in table1.

Table 1. Physicochemical characteristics of model oil [10].

№	Parameters	Quantity	Assignment Method
1	The amount of water in the sample, %	0.2	GOST 2477-65
2	Density, ρ_4^{20} kg/m^3	894.3	GOST 3900-85
3	Amount of paraffin, %	11.6	GOST 11851-85
4	Amount of resin, %	10.2	GOST 11851-85
5	Amount of asphaltene, %	5.2	GOST 11851-85
6	Freezing temperature, ^{0}C	16	GOST 20287-91
7	Paraffin saturation temperature of oil, ^{0}C	28	-
8	Melting point of paraffin, ^{0}C	57	GOST 11858-83
9	Amount of sulfur, %	0.22	GOST 1437-75
10	A/R	0.509	-

Difron-4201 produced by OJSC "EKOS-1" of the Russian Federation (table 2) was chosen as a depressant additive.

Table 2. Physicochemical characteristics of the depressant additive "Difron 4201" [10].

№	Indicators	Note
1	Appearance	Liquid from yellow to brown color
2	Density, 20 ^{0}C	Not more than 790 кg/m^3
3	Ignition temperature in a closed bowl	Not below (-28^{0}C)
4	Water solubility	Does not dissolves
5	Solubility in aromatic solvents	dissolves

The surface tension coefficient of the toluene solution of the test sample was experimentally measured using a tensometric device according to the ring detachment method (du Noüy); the relative error was ± 1%. The concentration of the solutions was gradually increased by the value of the surface tension coefficient of the samples reached a constant deal, and the final result was based on the surface tension of the solutions. During the experiment, water was used as the reference liquid. The measurement process was carried out at a temperature of 20 ° C, and the surface tension of the water was 72.75 mN / m.

The principle of operation of the tensiometer is to measure the force of separation of a wire ring made of a platinum-iridium alloy from the surface of the liquid under study. The calculation of the surface tension value in milliliters (mN / m) per meter is carried out using the following formula:

$$\sigma = \sigma_0 - n/n_0$$

where: n and n_0 - limbs, calculated in a scale proportional to the breaking force for the studied reference liquids; σ_0 - surface tension of the reference fluid[11-14].

Experimental part

The values of the surface tension coefficient of the depressant additive and asphaltene-resinous components of model oil of different concentrations in toluene studied in the laboratory conditions by the ring detachment method were determined, the results of the experiments provided in Table 3.

Table 3. Coefficient of surface tension of asphaltene components of the depressant additive "Difron-4201" and model oil, (MH / m)

Sample	Concentration,% (mass)				
	0.1	0.3	0.5	0.7	1.0
"Difron-4201"	34.8	39.2	40.1	40.12	40.12
Asphaltene	51.6	53.2	54.4	54.41	54.41
Resin	35.2	38.0	41.6	41.6	41.6

As can be seen from table 3, the value of the surface tension coefficient increases with an increase in the concentration of the additive, asphaltenes, and resin in the solution.

It is known that the value of the surface tension coefficient is small in non-polar liquids with weak intermolecular interactions and is broad in polar liquids [18].

Thus, the analysis of the experimental results shows that the value of the surface tension coefficient of the investigated depressant additive "Difron-4201" is less than the amount of the surface tension coefficient of the asphaltene and resin components of the model oil.

As a rule, under crystallization conditions, a complex structural unit (CSU) consisting of n-alkane nuclei is formed from a solution of a dispersed petroleum system. Such CSU has additional surface energy and therefore forms around itself a solvation coating of neutral components of the oil fraction and liquid n-alkanes [8]. As a result, an associative complex of paraffinic hydrocarbons with polar asphaltene-resinous components of a dispersed oil system with uncompensated surface energy is formed

The depressant additive is likely to weaken the molecular interactions between the CSU solvation coating components and the asphaltene-resinous components, resulting in a decrease in the aggregate stability of associations such as asphaltene-resin, but an increase in the tendency towards the association. They likely combine with each other, and the molecular interactions between the solvate coating and the asphaltene-resinous components are significantly weakened, which, in turn, leads to the transition of asphaltene-resinous associations into the composition of the precipitation. An associative complex characterized by low surface energy is formed between the CSU solvation coating and the polar group of the depressant additive polymer as a result of molecular interactions throughout the oil system. Thus, the system becomes thermodynamically equilibrium with a minimum of free energy.

Based on the foregoing, it was concluded that the value of the surface tension coefficient of the used depressant additive "Difron-4201" should be less than the value of the surface tension coefficient of polar asphaltene-resinous components of the dispersed oil system. This situation allows the depressants additives to form more thermodynamically stable associations with the CSU of the distributed oil system.

Considering that asphaltenes are the most polar components in the dispersed oil system, the value of their surface tension the coefficient will be greater than the value of the surface tension coefficient of all known additives. It follows that asphaltenes do not affect the effectiveness of the additives.

However, the value of the surface tension coefficient of the solution of the resin, components are closer to the amount of the surface tension coefficient of the additive solution. Consequently, the resin components of the petroleum system will affect the effectiveness of more additives.

Thus, laboratory experiments show that the value of the surface tension coefficient of asphaltene components of highly paraffinic model oil is significantly higher than the value of the surface tension coefficient of the Difron-4201 depressant additive and these components do not affect the effectiveness of the additive. However, the influence of the resin components on the efficacy of the additive is great and this effect increases as the value of the coefficient of its surface tension decreases.

Conclusions

Under laboratory conditions, the value of the surface tension coefficient of the "Difron-4201" depressant and asphaltene-resinous components of highly paraffinic model oil in a solution with toluene at the temperature of 20^0C was determined by the ring detachment method using a tensometric device, with a relative error of ± 1% and using water as reference fluid.

The results of laboratory experiments showed that the value of the surface tension coefficient of the asphaltene components of the highly paraffinic model oil is significantly higher than the value of the surface tension coefficient of the "Difron-4201" depressant additive and these components do not affect the effectiveness of the additive. However, the influence of the resin components on the efficiency of the additive is great, and this effect is enhanced as the value of the coefficient of its surface tension decreases.

REFERENCES

1. **Barskaya E.E., Ganeeva Y. M., Yusupova T.N., Dayanova D.I.** Prediction of problems in oil production based on the analysis of their chemical composition and physical and chemical properties // *Bulletin of Kazan Technological University*. - 2012.-V.15. -№. 6. -P. 166-169. (in Russian)
2. **Galimova G. A., Yusupova T. N., Ibragimova D. A., Yakupov I. R.** Composition, properties, structure and fractions of asphaltenes of oil dispersed systems // *Bulletin of the Technological University.* - 2015.- V.18. - No. 20.- P.60-65. (in Russian)
3. **Litvinets I.V., Nebogina N.A., Prozorova I.V.** Influence of additives on structural and mechanical properties of model oil systems // *Bulletin of the Perm National Research Polytechnic University.* Chemical technology and biotechnology. -2018. -No.3. -p. 42-55. (in Russian)
4. **Zhuravlev A.V., Pavlenina V.I., EPukhova E.Y.** Investigation of the influence of depressants on the low-temperature properties of oil and on the formation of asphalt-resin-paraffin deposits // *Bulletin of the Perm National Research Polytechnic University.* Chemical technology and biotechnology. -2019. -No. 2. P.104-112. *(in Russian)*
5. **Ismayilov G.G., Adygezalova M.B.** Impact of asphaltene concentration on macroscopic parameters of oil mixtures // *Herald of the Azerbaijan Engineering Academy*, 2020, V.12. № 3, p.77-81. *(in English)*
6. **Adygezalova M.B.** On the effect of oıl mıxıng on theır group structure // *Herald of the Azerbaijan Engineering Academy*, 2019, V.11, №2, p.57-62. *(in Azerbaijan)*
7. **Chen W., Zhao Z., Yin C.** The interaction of waxes with point depressant // *Fuel.* -2010. -V.89. -P.1127-1132. *(in English)*
8. **Xu J.** Effect of polar / nonpolar groups in comb-tupe copolymers on cold flowability and paraffin crystallization of waxy oils // *Fuel.* -2013.-V.103. -P. 600-605. *(in English)*
9. **Lyubimenko V.A.** Computer modeling of the structure and properties of intermolecular complexes in diesel fuels in the presence of depressant-dispersing additives *// Proceedings of the pussian State University of Oil and Gas named after I.M. Gubkin.* -2014. -No. 2. -P.44-51. (in English)
10. **Gurbanov G.R., Adygezalova M.B., Pashaeva S.M.** Influence of depressants on the formation of asphalt-resin-paraffin deposits in highly paraffinic oil // *Transport and storage of oil products and hydrocarbon raw materials*. -2020. -№1. -P.23-28. *(in Russian)*
11. **Ismailov O.Y.** Determination of the surface tension coefficient of liquid hydrocarbons // *II International Scientific and Practical Conference Bulatov readings*. -2018. -P. 114-116. *(in Russian)*
12. **Gashumova L.A., Nenakhova L.A., Zavodovsky A.G.** Determination of the surface tension coefficient at the oil - ASP solution by the rotating drop method // *Izvestiya vysshikh educational institutions. Oil and gas.* - 2014. № 5. P.10-15. *(in Russian)*
13. **Frolov V.I., Mi tyuk D.Y., Tverdiy R.E.** Methods for determining surface tension / Methodological instructions for a laboratory workshop on the course "Surface phenomena and dispersed systems". Moscow. 2013. - 46 p. *(in Russian)*
14. **Grigoriev B.V., Vazhenin D.A., Kuzina O.A.** Influence of the concentration of water solutions and temperature on the surface tension coefficient // *Bulletin of the Tyumen State University.* Physical and mathematical modeling. Oil, gas, energy. -2016.-V.2.-No. 3.-P. 35-48. (in Russian)
15. **Frantseva N.N.** Colloidal chemistry / Stavropol: *Publishing house Paragraph*. -2013.-56 p. *(in Russian)*

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