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RHEOLOGICAL ANALYSIS OF THE EFFECTIVENESS OF MODEREN METHODS OF INFLUENCING THE STRUCTURE AND CHARACTERISTICS OF OIL DISPERSION SYSTEM

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A B S T R A C T

If the amount of high-molecular components in oil transportation, group, structure and fraction composition, mixed in the analysis of other oils in laboratory analysis are correctly determined in the oil, it will be very effective in solving technological problems during transportation. On the basis of numerous studies the anomalous changes of rheophysicalfeatuuers of different crude oil mixes were investigated. It was defined that one of the main reasons for the anomaly is the variety of chemical composition and structure of miscible crude oils. We have established the mechanism of the effect of structural-group and fractionaloil content on its physicochemical properties and theological characyeristics resulting from a high content of high molecular components due to different solubility of liquid hydrocarbons relative to the latter ones.

1. INTRODUCTION

The viscosity of oils and petroleum products is quite complex, although this parameter standard is used to characterize these substances. Oil is multicomponent an unstable system containing hundreds of chemicals, which depending on ratios of concentrations to each other and external conditions (temperature, pressure) can exist as separate compounds and as complex complexes. This is in your own the queue greatly affects the physicochemical properties of oil, especially the viscosity.

Oil can be considered as an oil dispersion system, where the dispersed phase is asphaltenes, and the dispersion medium is resins, oils and light boiling fractions. The formation of the dispersed phase in oil dispersion system (ODS) is due to the different propensity of hydrocarbons and high molecular weight compounds for intermolecular interactions. Studies of the physical and chemical interactions of ODS components lead to the development of new theories related to the study of modern methods of influencing the disperse system in order to change the particle size and phase ratio of this system (Goroshko, 2003).

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Oil can be considered as an oil dispersion system where the dispersed phase is asphaltenes, and the dispersion medium is resins, oils and low-boiling. The theory of the formation of structural elements of oil dispersion systems of various types was put forward in the works, designating them as a complex structural unit (CSU), which is an element of a structure of mainly spherical shape, capable of independent existence under these constant conditions. In the composition of such a unit there is a core and a solvate shell surrounding the core. It is believed that the inner region of a complex structural unit is represented by a crystallite, an associate, or a gas phase bubble.

2. LITERARATURE REVIEW

For the first time, when studying the structure of asphaltenes, it was assumed that the core of the structural unit was formed by high-molecular polycyclic hydrocarbons and surrounded by components with a gradually decreasing degree of aromaticity. According to Unger F. G., mainly paramagnetic molecules are responsible for combining molecules into associations in ODS, and not heterocompounds and aromatic hydrocarbons.

Based on the studies, it was concluded that asphaltenes, resins, polycyclic aromatic hydrocarbons, solid paraffins and heteroorganic compounds have a tendency to structure in heavy oil residues (Sorokin & Khavkin, 2007).
In the works, the core of ODS is described as a mesh structure penetrated by diamagnetic molecules.

The size of the dispersed particles varies depending on the nature of the ODS. According to electron microscopy and X-ray radiation at low angles, the average particle size of straight-run distillate fractions is from 0.2 to 100 nm; purified oil fraction from 30 to 60 nm; vacuum distillates from tens to hundreds of nanometers, bitumen from 2.3-3.0 to 20-40 nm, and the structure itself consists of a set of quasi-spherical particles (Mineev & Boligatova, 2004).

Currently, the type of intermolecular bonds in oil associations and methods for evaluating them have not been definitively determined. The basis is the theoretical Lennard-Jones equations, describing the interaction of two molecules as the interaction of two microscopic balls, and the energy of intermolecular interactions is expressed as the potential of U (R) paired interaction of two particles depending on the distance R between them.

It is believed that a high degree of association of high molecular weight petroleum compounds is due to hydrogen bonds whose strength is 8-40 kJ/mol, while the strength of the Van der Waal bond is 8-12 kJ/mol (Persiyantsev, 2000).

To describe the structure of ODS, the work uses the theory of classical colloids, which is based on the assumption that the forces of the charging nature act between particles, and the models of associates are built with multiple charge layers that arise from the interaction of dipoles. Despite the absence of charged particles in ODS, an analogy can be drawn when constructing a model of homolite associations. So, the charging dipole moment in electrolytes is similar to the "spin dipole moment" in homoliths (Tronov, 1970; Kayumov et al., 2006). The free radical plays the role of a charged particle. A layer of particles having a spin moment is formed around it. A hedgehog-type structure is formed, which in turn is covered with a layer of spin-polarized particles, wherein antiparallel spin densities are directed in opposite directions (Figure 1). Interaction transfer is carried out in the spin system in the same way as charging (Sorokin & Tabakaeva, 2009).

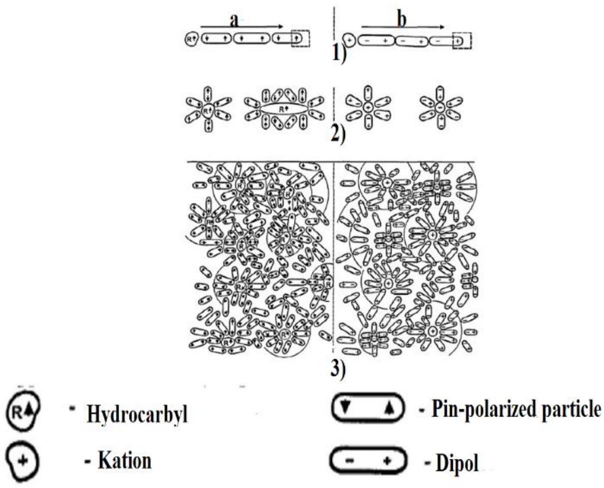

Figure1. Spin (a) and charge (b) models of molecular system interactions: 1) interaction transmission, 2) associative combination, 3) fragments of molecular systems

The stability of the entire associative system is supported by the stability of the direction of each spin in all molecules, and in the absence of an external orienting factor, ODS is not oriented (Nebogina et al., 2008). Also in the structural unit are elementary micro-regions (local formations and supramolecular structures), which are in a chaotic arrangement (Goroshko, 2003). It is considered that under the influence of certain external factors the system becomes more uniformly oriented, there are possible changes in the ratios of the components of the conditional core and the solvate shell, the packing density of molecular fragments in these areas, their strength, which generally leads to a change in their physicochemical characteristics.

Therefore, in order to reduce energy consumption and improve the quality of oil and petroleum products, possible applications of unconventional methods of affecting raw materials are being investigated, for example, the use of methods such as magnetic, electric, microwave, acoustic, laser, vibration, radiation treatment, as well as explosion energy, barrier discharge, ionizing radiation, low density plasma, etc (Sharifullin, 2006).

When studying the effect of ultraviolet irradiation and ozonation on the rheological properties of fuel oil and liquid bitumen, it was revealed that the transition of liquid from a quiescent state to a stationary state is accompanied by destruction of the spatial structure and breakdown of connections between associations.

In studies of the influence of the electromagnetic field, a technique was developed that allows determining the temperature of the beginning of the crystallization of paraffin in oils. Asphaltenes have been found to coagulate in the absence of aromatic hydrocarbons and to prevent intensive crystallization and separation of paraffin from solution while in colloidal state (Baimukhametov, 2005).

Based on the decrease in the energy of activation of the viscous oil flow, it was determined that the effectiveness of the influence of the magnetic field on the structure formation process of oil systems at temperatures from 20 °C to 60 °C depends on the ratio of benzene and alcoholic benzene resins included in the system - with a low content of alcoholic benzene resins, the decomposition of complex structural units and a decrease in rheological parameters.

Perhaps, when applying an external magnetic field, the orientation of spins occurs, the location of which at rest is chaotic, and the stronger the magnetic field, the higher the level of ordering of the chemical system can be achieved (Goroshko, 2003).

The work found that magnetic treatment of oil leads to an increase in the number of antioxidants in ODS, which is evidence of prevailing dissociation processes leading to the emergence of new inhibitory centers preventing the development of radical-chain oxidation processes. Inhibitory centers are paramagnetic molecules that make up the nucleus of the aggregative combination.

The application of an external magnetic field to the ODS leads to a change in the direction of spins in all molecules and a violation of the stability of the system, which is manifested in the polyextractive dependence of the change in paramagnetic, antioxidant and rheological properties on the relaxation time. It was found that the properties of paraffin oils under the influence of a magnetic field vary slightly, while the properties of viscous oil with a high content of resinous-asphaltenes undergo strong transformations of the structure, which are mainly associated with the process of decay of associates and molecules, accompanied by the formation of new antioxidant and paramagnetic centers, and a decrease in viscosity (Zevakin & Mukhametshin, 2008).
When studying the change in the energy state of the oil system under ultrasonic influence on the basis of a change in the concentration of paramagnetic centers (PCS) at various temperatures, the processes of compaction of supramolecular structures and the redistribution of hydrocarbon particles were revealed.
A significant decrease in viscosity and a decrease in oil density is a result of ultrahigh-frequency radiation treatment, while the H:C ratio increased slightly (Sharifullin et al., 2006).

It has been found that short-term microwave exposure to bituminous rocks increases the yield of the extract, in which the proportion of hydrocarbons increases, the degree of aromaticity and oxidation and the content of asphaltenes decreases. Prolonged exposure leads to a decrease in the extraction of organic matter and the formation of insoluble substances (Sergienko, 1959).

In the study of the change, it is assumed that such an effect leads to the destruction of the supramolecular structure of asphaltenes, as a result of which they lose part of their mass in the form of an organic extract, and the structure itself acquires a more carbonized character. Upon irradiation with light of resinous-asphaltenes, degradation and oxidative transformations were observed to form a gas phase and highly fusible organic solvent insoluble compounds that turned out to be more paramagnetic than the original components (Ibragimov et al., 1986).

When examining the effect of heat treatment on the rheological properties of oil, a sharp increase in viscosity values was revealed at a subsequent decrease in temperature to the initial state.

The effect of solvents on the paramagnetic properties of native and secondary asphaltenes was studied using the example of chloroform, alcohol, benzene, toluene, n-heptane (Petrova et al., 2005). It has been found that solvents can have a "negative" effect by reducing the number of paramagnetic centers (PMC) (paraffinic hydrocarbons (n-heptane), chloroform and a mixture of alcohol and benzene), or increase the concentration of PMC by producing a "positive" effect (aromatic hydrocarbons (benzene and toluene). The number of asphaltenes interacting with PMC varies depending on the nature of the sample and the solvent, and in asphaltenes of secondary origin these changes are more pronounced, possibly due to the thermal effect to which oil is subjected during processing, which contributes to the formation of new centers in secondary asphaltenes (Ibragimov, 2003).

In the paper, the use of an aqueous solution of the polymer of sodium salts of polycarboxylic acids as a method for improving the characteristics of water-nitrogen emulsions was investigated, the result of which is an increase in the durability of the emulsion without release of water at a temperature of 15-30 °C (Sharifullin 2006).

For a better comparison of synthesized substances as oil viscosity control additives, efficiency indices calculated additives according to the formula:

$$J_{eff} = \eta_n/\eta_{im}$$

Jeff - index of additive efficiency;
η_n - dynamic viscosity of the initial oil, Pa·s;
η_{im} – dynamic viscosity of oil with additive improver, Pa·s.

J_{eff} Additive Performance Index shows how many times dynamic viscosity of oil with additives of investigated additives differs from dynamic viscosity of the source oil. The greater the index value efficiency of J_{eff}, the higher the ability of the additive to be studied to improve rheological properties of oil.

3. RESEARCH METHODOLOGY

The formation of structured oil systems depends on the content (volume fraction) of particles in oil, the distances between them and the interaction forces of particles, since for aggregation of particles an important condition is the probability of their collision and the presence of a coagulation structure of the forming aggregates (Sharifullin et al., 2006).

Oil dispersions can create aggregates with solid pore walls porous formation and with other solid particles contained in oil. The change in mass of non-deformable nanoaggregates is defined as.

$$\frac{dm}{dt} = (m\infty - m)\omega$$

The solution to this equation is represented as

$$m = m_\infty [1- \exp(- \omega t)]$$

Assuming that the nanoaggregates have a spherical shape and that $m = \pi/6 \cdot \alpha^3$ determine the size of the nanoaggregates based on the expression for the particle collision frequency.

Our research gives us reason to believe that the correct regulation of the reaophysical and chemical properties of oils should be carried out only after the determination of laboratory results of high-molecular components and quality bank (Ismayilov et al., 2016).

We analyzed the rheophysical and chemical properties of oils extracted from different oil fields of Azerbaijan (Table 1, 2).

As can be seen from Table, the amount and fractional composition of high-molecular components in oils are closely related to the rheophysical and chemical properties of oils (Usubaliev et al., 2015).

Table 1. Rheophysical and chemical properties of oils extracted from different oil fields of Azerbaijan

Indicators	Bulla	Balakhani heavy	Surakhani
Resin, mass. %	9,6	16,2	14,3
Asphaltenes, mass. %	0,22	2,8	2,68
Waxı, mass. %	13,1	0,31	1,9
Determination of kinematic viscosity, sSt			
0 ^{0}C-də	88,7	231,3	68,4
10 ^{0}C-də	48,4	197,8	36,9
20 ^{0}C-də	23,2	160,3	20,2
30 ^{0}C-də	14,6	112,7	11,3
40 ^{0}C-də	6,1	41,4	5,2
50 ^{0}C-də	3,2	18,2	2,8

The temperature factor has a different effect on such oils, and it is more appropriate to analyze them in terms of structure. Although paraffin, resin, and asphaltenes are similar in quantity in such oils, their structural differences lead to anomalies in the oils (Nurullayev et al., 2016). Although certain quality indicators of oils are subject to the rule of additiveness when mixed with each other, rheophysical-chemical parameters do not follow this rule. This can be seen in the mixture of oils (Nurullayev, 2016). A significant content of solid hydrocarbons and high molecular weight compounds in the oil causes the presence of the crystallization start temperature (liquidus) when the thermodynamic state of the dispersion system changes, which depend on the concentration of solid paraffins, resins and asphaltenes, as well as their relationship with each other.

Table 2. Rheophysical and chemical properties of oils extracted from different oil fields of Azerbaijan

Indicators	1:1 in propor-tion, Bulla: Balak. heavy	1:1 in propor-tion, Surakhani: Balakhani heavy	1:1 in propor-tion, Surak.: Bulla
Resin, mass. %	8,9	15,7	11,3
Asphaltenes, mass. %	1,78	2,72	1,69
Waxı, mass. %	6,92	1,43	8,65
Determination of kinematic viscosity, sSt			
0 ^{0}C-də	243,9	223,6	112,5
10 ^{0}C-də	211,3	204,3	86,8
20 ^{0}C-də	97,8	89,4	46,5
30 ^{0}C-də	52,4	45,6	24,1
40 ^{0}C-də	34,8	31,2	13,2
50 ^{0}C-də	12,6	8,7	5,8

Thus, considering that oil is a multicomponent thermodynamically and aggregatively unstable ODS, in which, when conditions change, the processes of association of components increase due to strengthening intermolecular bonds between them, it becomes important to study the structure in ODS in a wide range of temperatures and shear rates, which will determine the optimal conditions for the production and transportation of ODS of various nature (Usubaliev et al., 2015; Nurullayev 2016).

4. RESEARCH RESULTS AND DISCUSSION

Studies have revealed that in the presence of resins, solid hydrocarbons crystallize in a dendritic (aggregate) form, which is characterized by the isolation from the solution of unfinished single crystals formed at many centers. Increasing the content of resins in the system helps to slow down the growth of crystals, as well as deformation of their surface and the emergence of new crystallization centers on them. Figures 2, 3 show how the quality of mixtures in the example of Azerbaijani oils depends on the initial properties of the oil. In some cases, abnormal changes in the quality of the oil during mixing, and some mixtures have been found to cause specific problems.

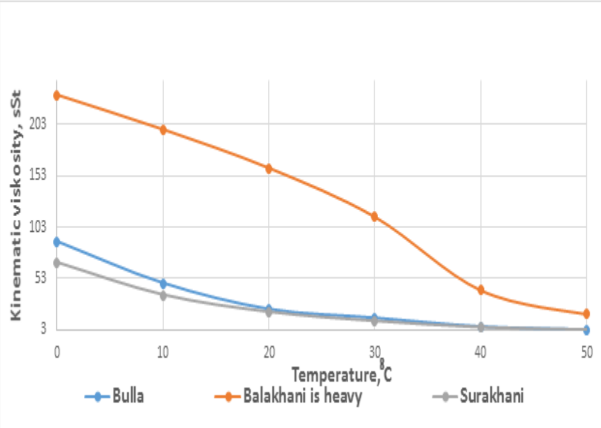

Figure 2. Rheophysical and chemical properties of oils extracted from different oil fields of Azerbaijan

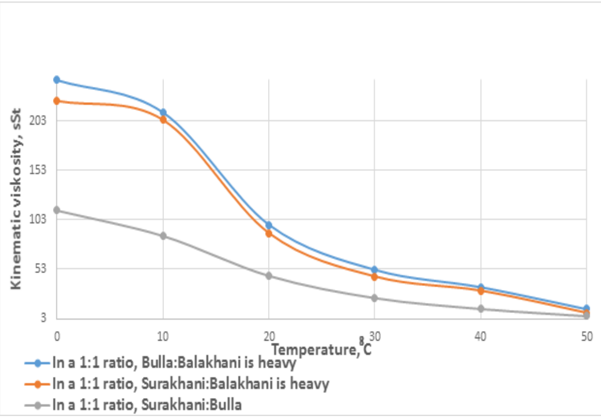

Figure3. Rheophysical and chemical properties of oils extracted from different oil fields of Azerbaijan in different proportions

Asphaltenes in a dispersed state can play the role of primary centers of crystallization of solid paraffins, and in colloidal - prevent the aggregation and precipitation of paraffin crystals.

The work suggest that the main reactions leading to the formation of asphaltenes (under oil distillation conditions) are fragmentation reactions of multi-block molecules.

When studying the behavior of the liquidus line of binary systems and comparing experimental and calculated values, a significant difference in the results obtained was revealed, which thus necessitates the use of equations describing the course of the liquidus lines of the binary systems under consideration, including correction factors.

The inadmissibility of the application of the additive rule to such mixtures should be taken into account, and it should be considered necessary to carry out preliminary laboratory tests in order to obtain rational mixtures.

5. CONCLUSION

As a result of laboratory studies, it was determined that the chemical composition of oil mixtures significantly affects the rheophysical properties. During the process, the amount of high-molecular components changes depending on their structure. The main reason for this is due to the structural variability of high-molecular components and the fact that the micropores between the molecules they contain have a different structure before the process. Depending on the size of these pores, the amount of resin, asphaltene and paraffin absorbed varies.

Ways to overcome the complications of production, transportation and even processing of anomalous oils and natural bitumens are to improve their rheophysical and chemical properties, which requires extensive research, all the features of a complex system such as oil must be sought in the amount of the individual components that make them up, and in the general structure of the oils themselves, in the proportions of the components.

It was found that the rheophysical chemical properties of paraffin, resin-asphaltene anomalous and heavy oils can be adjusted by adding additives or light oils, and the viscosity and density of the additives added during this process do not play a major role. The main condition here is the hydrocarbon content of the added components. The amount of high-molecular components during transportation in individual and mixed oils in the laboratory, the correct determination of the group, structure and fraction composition, can be very effective in solving technological problems that arise during transportation.

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References:

Baimukhametov, M. K. (2005). Improved technologies to combat the asphalt, resin, and paraffin deposits in oilfield systems in the fields of Bashkortostan. Ph.D. Thesis. Russia, Ufa, 204, 176-182.

Goroshko S. A. (2003) Effect of inhibitors of wax on the efficiency gas transport at “Pribrezhnoe” field. Ph.D. thesis. Russia, Krasnodar, 201, 176-181.

Ibragimov, G. Z., Sorokin, V. A., & Khisamutdinov, N. I. (1986). *Chemical reagents in petroleum production: Handbook*. Moscow: Nedra, *240*, 156-165.

Ibragimov, N. G. (2003). Petroleum production problems. *Ufa, 302*, 198-204.

Ismayilov, G. G., Nurullayev V. H., Musaev S. F., (2016) The prediction of water cutting and density of oil water condensate mixes. *International journal of engineering sciences and research technology, India, 8*, 768-775.

Kayumov, M. Sh., Tronov, V. P., Gus'kov, I. A., & Lipaev, A. A. (2006). Account of the features of formation asphaltene deposits in the late stage of development of oil fields. *Neftyanoe khozyaistvo, 3*, 48-49.

Mineev, B. P., & Boligatova O.V., (2004). Two types of paraffin, the drop-down on the downhole equipment in oil production. *Neftepromyslovoedelo, 12*, 41-43.

Nebogina, N. A., Prozorova, I. V., & Yudina, N. V. (2008). Features of the formation and precipitation of water-oil emulsions. *Neftepererabotka i neftekhimiya, 1*, 21-23.

Nurullayev, V. H. (2016). The basis of physical and chemical properties of oil produts and their regulation at consecutive transfer. *Research journal of chemical and environmental sciences, 1*, 35-42.

Nurullayev, V. H. (2016). Improved measurement method of physical and chemical properties of oil products by fewer tests. *International Journal of Petroleum and Geoscience Engineering, USA, 2*, 66-77.

Nurullayev, V. H., Gahramanov F. S., & Usubaliyev B. T. (2016). Education mechanisms cavitational zones by menas of asphalten-pitch-wax deposits on a surface to a pipelines. *International journal of engineering sciences and research technology, 1*, 441-447.

Petrova, L. M., Fors, T. R., Yusupova, T. N., Mukhametshin, R. Z., & Romanov, G. V. (2005). Effect of Deposition of Solid Paraffins in a Reservoir on the Phase State of Crude Oils in the Development of Oil Fields. *Petroleum Chemistry, 3*, 189-195.

Persiyantsev, M. N. (2000). *Oil production under complicated conditions*. Moscow: Nedra-Biznestsentr. 653, 347-362.

Sergienko, S. R., Taimova B. A., & Tatalaev E. I. (1959). *High-molecular non-hydrocarbon compounds of oil*. Moscow: Nauka, pp. 367-372.

Sorokin, S. A., & Khavkin S. A. (2007). Features of physical and chemical mechanism of production asphalted, resinous and of paraffin formations in the wells. *Burenie i neft, 10*, 30-31.

Sorokin, A. V., & Tabakaeva A. V. (2009). Influence of the gas content in petroleum on ARDO formation in the well lift. *Burenie i neft, 2*, 25-26.

Sharifullin, A. V., Baibekova, L. R., Suleimanov, A. T. (2006). Features of the structure and composition of oil deposits. *Oil Gas Technol., 6*, 19-24.

Sharifullin, A. V., Baibekova, L. R., Khamidullin, R. F. (2006). Composition and structure of asphalt-resin-paraffin deposits of Tatarstan. *Oil Gas Technol., 4*, 34-41.

Sharifullin, A. V., Baibekova, L. R., Suleimanov, A. T., Khamidullin, R. F., Sharifullin V. N. (2006). Features of the structure and composition of oil deposits. *Oil Gas Technol., 6*, 19-24.

Tronov, V. P. (1970). *Mechanism of formation of resin-wax deposits and their prevention.* Moscow: Nedra. 192, 69-74.

Usubaliev, B. T., Ramazanova, E. E., & Nurullaev, V. H. (2015). The use of nanostructured coordination compounds to reduce viscosities of heavy commercial oils during transportation. *Problems of collecting, preparing and transporting oil and oil products, 3*, 117-126.

Zevakin, N. I., & Mukhametshin R. Z. (2008). Paraffin deposits in formation conditions of horizon D1 Romashkinskoye field: *Proceedings of TatNIiPINeft. VNIIOEG, 176*, 134-145.

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