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Analysis of the Mechanism of Action of Chemical Reagents against Asphaltene-Resin-Paraffin Depositions Using Modern Methods on the Example of Azerbaijan Crude Oils

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ABSTRACT

In the equipment operated in the oil industry, the formation of a solid layer of ARPD on the inner surface of the pipes causes the precipitation of salts and the formation of an aggressive environment, which leads to corrosion of the equipment and its rapid failure. There are many studies on the fight against paraffin deposition. Based on the results of these studies, the mechanism and conditions of paraffin deposition have been studied, and methods and measures for combating it have been developed. Nevertheless, the elimination of problems caused by paraffin deposition during the movement of highly paraffinic oils remains relevant. Therefore, the development of new physicochemical methods in the fight against ARPD is of great importance. In the article, a new method is proposed for testing paraffin deposition inhibitors, taking into account the structural and energy properties of oil. The study of the effect of chemical reagents, magnetic and cavitation environments on the structural and rheological properties of Azerbaijani crude oil, depending on the amount of tar-asphaltenes-paraffins, was conducted.

1. INTRODUCTION

Recently, the amount of resin-asphalten-paraffin, high-freezing point and degassed oils has begun to increase in the oil fields of the world's oil-producing countries. During the operation of such facilities, thermobaric conditions change due to the opening of the reservoir, which leads to the phase transition of paraffin hydrocarbons. The phase transition leads to the formation of asphalt, resin and paraffin deposits (ARPD) in the pumping equipment of deep underground wells and surface communications. The formation of ARPD leads to a decrease in well production, the implementation of major repairs earlier than scheduled, deterioration of transportation and an increase in the risk of accidents. Currently, one of the most effective methods of combating paraffin deposits that cause the formation of ARPD is the use of chemical reagents that reduce the saturation temperature of oils with paraffins, which are in liquid and solid forms depending on their aggregate state.

The research studies considered methods for assessing the effectiveness of paraffins in oil with chemical reagents using the universal physical parameter E^{α} of the condensed activation energy of oil hydrocarbons. Activation energy characterizes the potential energy of intermolecular interactions (IMI) and determines the breakdown of the characteristic microstructural order and stability of the oil disperse system as a whole under the influence of the average thermal energy kT of the thermal Bronn motion.

2. LITERARATURE REVIEW

The nature of the activation energy depends on the formation of weak hydrogen bonds, orientational and dispersion forces in hydrocarbons [1]. The energy E^{α} determines the average "settled" existence time of liquid molecules τ0t described by the Arrhenius equation:

$$\tau 0 = \exp\left(E^{\alpha}/kT\right) (1) \qquad (1)$$

where τ0 is the wave period at equilibrium; k is the Boltzmann constant, T is the temperature. In experiments, the activation energy is determined by the nuclear magnetic resonance (NMR) method.

In general, E^{α} characterizes the dissociation energy of weak hydrogen bonds and plays the role of a function of the structural molecular parameters of the system and manifests itself in the type of bond, the shape and size of molecules, the component composition of the dispersed medium, etc., and does not depend on temperature, type of equipment and experimental conditions [2].

Analyses of dispersed oil systems have shown that if the internal structure of the oil dispersed system (ODS) changes at the molecular level as a result of physical and chemical effects, the activation energy of the oil also changes accordingly. On the other hand, the level of E^{α} reflects the condensed system in equilibrium [3]. Using a modern method, the effectiveness of the interaction of oil with chemical reagents "Ef" is determined by the following formula

$$E_f = (E_a^{kr} - E_a^{initial}) \cdot 100\% / E_a^{initial}$$

where E_a^{kr} is the activation energy of the chemical reagent treated with oil, $E_a^{initial}$ is the activation energy of the oil without the reagent. A comparison with the well-known gravimetric method for determining paraffin deposits on a cold metal surface showed that the average relative error between the two physically different methods is 22.6% and the correlation coefficient is 0.964. In addition, this method significantly saves the amount of oil and chemical reagent and does not impose any restrictions on the high viscosity of the oil, the maximum amount of asphalt-rezin-paraffinic substances in its composition [4].

The reason for the formation of oil emulsions is the effective mixing of oils with produced water at the mouth of the well during its rise to the surface and their subsequent action on the field communications [5]. The most common emulsions in the oil and gas industry are water emulsions in oil. The presence of surfactants in oils, such as asphaltenes, paraffins, resins and naphthenic acids, causes the dispersion of water droplets in the oil [6]. Such substances are dependent on oils. The concentration of existing natural substances that affect the stability of water-oil emulsions is higher in heavy oils than in light oils. The preparation of oil in the fields is one of the main processes associated with the production, collection and transportation of commercial oil to the consumer - refinery or export. The efficiency and reliability of the main transport pipelines depends on the quality of the prepared oils [7].

In the final stages of oil production, the amount of water in the oil can be 90% or more. In this case, the raw materials included in oil refineries are not only characterized by a variety of physical and chemical properties, but also change its composition over time.

The issue of reducing energy costs in oil storage systems remains relevant and is partly due to the formation of sustainable high-viscosity emulsions. Therefore, its solution depends significantly on the efficiency of the decomposition of water-oil emulsions. The increase in the production of heavy and high-viscosity oils, capable of forming sustainable emulsion systems, requires the improvement of traditional technologies and the preparation of hydrocarbons for further processing. Complications during the dehydration and desalination of such oils, as a rule, occur in the presence of various types of mixtures, which must also be removed by the most effective methods. An important aspect in the preparation of similar oils is the development of composition demulsifiers. The main requirements for such reagents are efficiency at low temperatures and good dehydration dynamics of durable water-oil emulsions.

The use of compositions is more effective than the use of any compound in its pure form. In this regard, the development of relatively effective composition demulsifiers is very important. The purpose of the study is to study the effectiveness of composition demulsifiers in the laboratory for the decomposition of sustainable water-oil emulsions [8].

3. RESEARCH METHODOLOGY

Solving such problems using scientific provisions of various fields of science mechanics, molecular physics, physical and colloidal chemistry, which ultimately led to the creation of a new general scientific direction of physical and chemical mechanics. Physical-chemical mechanics is defined as a science that studies the laws of molecular mechanism of formation of spatial structures in disperse systems, as well as processes deformation and destruction of such structures, solids and materials depending on combination of physicochemical and mechanical processes [9]. Considering that most real solid and liquid materials represent various types of colloidal systems, the development of the main problems of physicochemical mechanics is closely connected, primarily with such sections of modern colloidal chemistry as physical chemistry of surface phenomena and disperse systems, structuring in disperse systems and solutions high molecular weight compounds [10].

Oil and petroleum products are typical under certain conditions colloidal systems called petroleum disperse systems, study which are necessary for the skilled organization of their production, transport and processing. Diversity and specificity of issues arising in the study of oil disperse systems, anomalies in the behavior of the latter made it necessary to consider them in a special section of science - physicochemical mechanics of oil dispersion systems and developed on this basis of the theory of controlled phase transitions in oil systems. One way to improve the transport properties of high viscosity and high stagnation petroleum is the introduction of synthetic components into their composition, which can be low-molecular olefins, long-chain alpha-olefins and their co-oligomers are used. At the same time, long-chain alkyl radicals act as carriers of depressant properties, aromatic hydrocarbons with long alkyl radicals and heterocyclic connections. The longer the carbon chain of paraffin hydrocarbons depressant additives, the greater the depression of the freezing temperature they cause. Development of depressant additives based on cheap and affordable raw materials and characterized by good viscosity-temperature properties, is an urgent task.

In industrial conditions, generally technical mixtures of alpha-olefins are used. Obtained either by cracking paraffins or by oligomerizing ethylene. Invention proposes a depressant additive based on ethylene-propylene copolymer, and also in combination with various compounds whose structure promotes development dispersing properties. Such compositions significantly improve low temperature characteristics of diesel fuels and low-temperature and viscous properties of oil oils.

As a result of the volumetric action of the depressor additive molecule due to the high polarity functional groups form their own associations and micelles at temperatures greater than higher than the associative temperature of normal paraffin molecules. Such micelles contain polar groups within the association, and aliphatic radicals are directed to the dispersion Wednesday. This promotes the solvation of micelles with molecules of normal paraffin hydrocarbons and creation of amorphous structures. Their crystallization in cooled oil dispersions systems are localized, and during condensation large, weakly connected are formed with each other dendrites. Thus, the participation of such solvated structures in education continuous spatial meshes in solution begin at lower temperatures. Foreign synthetic additives (R-140, GY-3, Danox-501, DMN-2005 and AR-174) have a high cost. In this regard, relevant for Azerbaijan remains the choice and development of effective additives, which in addition to quality indicators will increase the economic effect, defined as the cost of the reagent, and the introduction of oil preparation and transportation into the system.

The known depressors include Paraflow AzNII, alkylphenol IPX-9, Dorad-1A, VEO-504 Tyumen, Azolat-7. These include metal salts, salts of higher synthetic fatty acids, silicate-sulfonate solutions, and sulfated alkaline lignin. Currently, the following reagent grades used: butylbenzene fraction (butylene benzene, isopropylbenzene, polyalkylbenzenes). A toluene fraction (toluene, isopentane, n-pentane, isoprene), SNPCH-7p-1 is a mixture of paraffinic hydrocarbons of normal and isostructural, as well as aromatic hydrocarbons (OJSC "NIIneftechem", Kazan), SNPCH-7r-2-hydrocarbon composition consisting of their light pyrolysis resin and hexane fraction (JSC "NIIneftechem", Kazan), HPP-003, 004, 007 (ZAO Kogalym Chemicals Plant, Kogalym), ML-72 - mixture synthetic reagents, SNPCH-7200, SNPCH-7400 reagents - complex mixtures of oxyalkylated surfactants and aromatic hydrocarbons ode (OJSC NIIneftechem, Kazan), ICB-4 reagent, which has a complex effect on ARPD and corrosion of metal pipes (INPP, Ufa), INPAR (Neftechem Experimental Plant, Ufa), SEVA-28 - copolymer of ethylene with vinyl acetate (VNIINP and VNIIneft, Moscow). In addition to the listed reagents of oil and gas production, Ural-04/88, DM-51; 513; 655; 650, DV-02; 03, SD-1; 2, O-1, B-1, XT-48, ML-80, Proqalit GM20 / 40 and HM20 / 40. Along with the high cost, a significant shortcoming of the chemical method is the difficulty in selecting an effective reagent, due to the constant change in operating conditions during the development of the deposit.

The study of physicochemical characteristics and component composition of oil allowed identify natural depressants from among the Azerbaijani oils. They are characteristic of low paraffin content, low resin content and high naphthenic content hydrocarbons. A significant characteristic of such additives is their surface the activity, i.e. the effectiveness of the additive is due to some active component; included in its composition, and prone to intermolecular interactions with certain components of the foreground system. Also with the participation of the author developed compositional additives as a depressant additive for transporting oil and oil mixtures.

4. RESEARCH RESULTS AND DISCUSSION

Studies have shown that the efficiency of activation energy after the addition of chemical reagents to the volume of oils leads to a positive result of 10-33%. Fig. 1 shows a comparison of the combined effect of activation energy, cavitation and magnetic field (Fig. 2) on the formation of ARPD of chemical reagents in oil [11, 12].

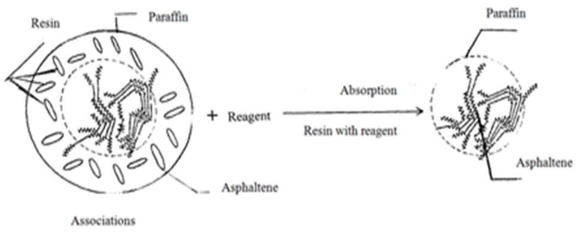

Fig. 1. Combined effect of activation energy, cavitation, and manganese field on the formation of ARPD of chemical reagents in oil.

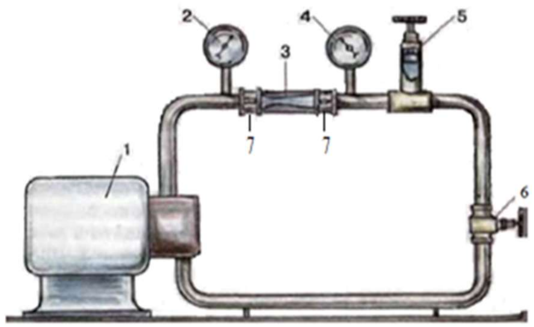

Fig. 2. 1-Pump (BALDOR, V=110-220, A=5,2-2,6, F.T.=1475 min-1, W=770), 2,4-manometers, 3-collapsible cylinder-shaped cavitator, 5-static pressure regulator, 6-throttling valve, 7-magnetic actuators.

When considering the process of paraffin precipitation to analyze the mechanism of action of the chemical reagent, it was determined that at cold temperatures in oil, the formation of monocrystallization centers of paraffin nuclei begins. With the decrease in tar in oil, the viscosity should decrease sharply, but this does not happen during the process.

This is explained by the fact that after the oil associates that cause an increase in viscosity in oils are absorbed by the resin reagent, the process of asphaltene association with paraffin occurs, which does not allow the viscosity of the oil to decrease (Fig. 3).

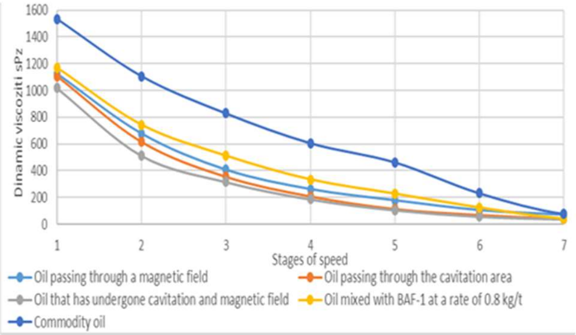

Fig. 3. Analysis of the rheological properties of Muradkhanli oil mixed with BAF-1 reagent after exposure to magnetic and cavitation environments.

In order to prevent such a process in the oil industry, it is necessary to add chemical reagents, and it is considered more expedient to have this additive as condensate. When analyzing the effect of the chemical reagent in Muradkhanli mixed oil together with cavitation and the manganese field, it was determined that during the process, the physicochemical properties of oil and tar-asphaltene-paraffin precipitation are observed with different results (Fig. 4).

The magnetic activator is similar in its technical characteristics to magnetic activators used in oil production. The actuator uses a seven-ring magnetic system, and in the space between it and the magnetic field of the body, it is possible to obtain several zones with changing radial directions. A Venturi tube-based cavitator was used to create the cavitation process.

To analyze the mechanism of action of chemical reagents, let us consider the process of precipitation of tar-asphaltenes-paraffins. When the oil is supercooled below morphological stability, the formation of individual crystallization centers - paraffin nuclei occurs spontaneously (self-assembly or conustruction).

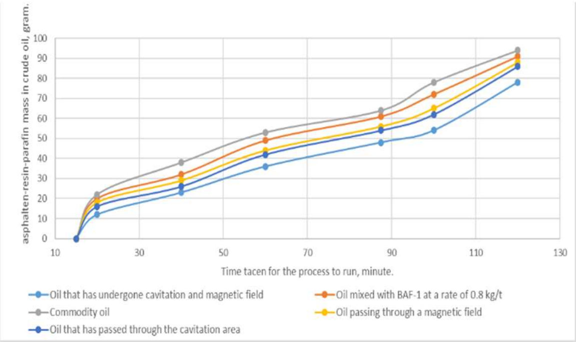

Fig. 4. Analysis of resin-asphaltene-paraffin formed in Muradkhanli oil at a temperature of 5 ^{0}C after exposure to chemical reagents, magnetic and cavitation environments.

Paraffins (mainly C17-C36) differ from all other hydrocarbons in that their molecules, during crystallization on a metal surface, form a dense layer-by-layer, thread-like zigzag meander-shaped configuration.

Table 1. Physical and chemical characteristics of Muradkhanli mixed oils (commodity).

Physico-chemical indicators	Results				
	Crudoil	Reag.	Mag. effect	Cav. effect	Mag. cavi. effects
Density, kg/m^3	876.7	875.9	874.4	873.8	873.6
Viscosity, mm^2/sec.	83.32	62.3	68.7	64.5	64.2
Resin, %-mas.	18.32	9.85	11.43	10.76	10.42
Asphalten, %-mas.	4.86	5.32	3.91	3.28	3.25
Paraffin, %-mas.	6.21	8.43	7.34	5.17	5.12

Due to the local fluctuation of the oil due to cooling, a new phase arises in the metastable state of the system, during which the solution is supersaturated with paraffins. A distinction is made between subcritical, critical and supercritical sizes of resin-asphaltenes-paraffin particles. The driving force of the paraffin crystallization process is the difference in chemical potentials between the nucleus and the initial phase. The fluctuation nucleus of a new phase is associated with a change in the Gibbs free energy. An additional factor affecting the intensity of paraffin deposits is the presence of resin-asphaltenes in the oil. Experiments show that the addition of resin-asphaltenes to oil leads to a monotonous increase in solid asphaltene-resin-paraffin deposits, for example, when 8% (by mass) of resin-asphaltenes is added to oil, the amount of solid resin-asphaltenes increases from 20 to 48 g/m2, i.e. 2.2 times.

This is due to the fact that during the phase transition of hydrocarbons, polar asphaltenes and resins are adsorbed on the edges of rapidly growing paraffin crystals and, together with large-volume associations, cause the formation of heterocomplexes, closing the paraffin voids. Chemical reagents are added to oils to protect the resin-asphaltene-paraffin from precipitation. When a chemical reagent, which is a surfactant, is dissolved in oil, the dispersed system is brought to a new thermodynamic equilibrium state and changes the internal structure of the liquid. It should be emphasized that real oil cannot correctly demonstrate the result of the theoretically calculated reaction of the chemical reagent with experimental results. The results of our studies have shown that the amount of resin-asphaltene-paraffin precipitates formed during the interaction of oil with various chemical reagents depends not only on the effectiveness of the reagents' action ("Ef"), but also on the potential energy ΔE of the medium acting on them. Potential energy depends on the ratio of the amount of resin-asphaltene-paraffin formed in oil under the influence of the chemical reagent to the amount formed without the reagent, Y.

$$Y = m^{reag}/m^{initial} \tag{3}$$

$$\Delta E = (1- Y)/U \tag{4}$$

Here U is the activation coefficient of oils, determined according to temperature and activation energy. As a result of the study of Muradkhanli oil, it was determined that the amount of tar-asphalten-paraffin deposits formed on the metal surface at low temperatures is inversely proportional to the difference in activation energy of hydrocarbons in the oil ΔEa = (Earea – Eainitial). As can be seen in Fig. 3, the effect of various physicochemical methods on Muradkhanli oil is fundamental. If the difference ΔEa has a positive value (increase), then a monotonous decrease in the surface AQPÇ occurs, if the difference ΔEa has a negative value, on the contrary, an increase occurs in the solid phase of deposits, and in this case the function takes the form Y(ΔEa)=1. When ΔEa>0, the strength of hydrogen bonds of hydrocarbons in a dispersed medium increases, which in subsequent stages causes crystals to grow naturally in paraffin hydrocarbons. This process leads to the slowing down and blocking of the growth of paraffin nuclei to a stable critical size. At the same time, solid paraffin associations form a thinner adsorption layer on the metal surface. The effect of chemical reagents depends on the mechanism of structure formation of oils, on the initial intermolecular forces of interaction (IMFI). The component composition of oils is characterized by a high value of the ratio of resin and asphaltene Cres/Casp. Polar inhibitors dissolved in oil are adsorbed at the boundary of the solvate clouds of internal adsorption-solvate complexes (ASC) and transfer oil dispersion systems to a higher potential energy level. It was found that the higher the characteristic ratio Cres/Casp, the higher the effect of the reagent (shift of ΔEa to the upper limit), as can be seen in Fig. 3. The negative effect occurs in oils with a high bulk energy of the IMFI and a low Cres/Casp ratio. One of the possible mechanisms for increasing Earea in oils is the process of dissolving the ASC nucleus in aromatic hydrocarbons. Paraffin deposition inhibitors usually consist of surfactants, light or heavy pyrolysis resin organic solvents consisting of 70-86% arene hydrocarbons, which affect the destructiveness of asphaltenes in them. The dispersion process is accompanied by a decrease in the linear dimensions of the ASC core, which leads to an increase in the specific surface area of the internal adsorption centers and, accordingly, an increase in the orientation polarity (orderly and stable) with an increase in the coordination number of molecules near the ASC. Studies have shown that chemical reagents for reducing ARPD occur more effectively at relatively low values of the activation energy of oil (11-16 kC/mol) under the influence of a modifier (cavitation or magnetic fields) (Pivovarova . et al. 2002). If the initial energy is above Eainitial>18 kC/mol, then the chemical reagent will lead to a negative effect, i.e. when the oil temperature decreases, the natural selectivity of ARPD is stimulated.

5. CONCLUSION

The reason for this is the decrease in the phase transition energy of paraffins, and the decrease in temperature in oil creates conditions for the formation of new crystals of paraffin molecules. One of the main conditions for selecting and applying a chemical reagent to reduce the ARPD is to maximize the activation energy of hydrocarbons in the oil. The structural-energetic approach to selecting a chemical reagent against paraffin deposition. The correct selection of the object (physical area for supplying the reagent to the system) and the petrochemical reagent pair for cleaning oil pipelines can significantly increase the efficiency of the technological process. The use of new high-energy reagent compositions for supplying chemical reagents to the system, using the effects of magnetic and cavitation environments, has been proposed by us as an effective method for protecting against ARPD.

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