REPUBLIC OF AZERBAIJAN

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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

RESEARCH AND APPLICATION OF NANOTECHNOLOGY AGAINST COMPLEXITIES IN OIL REFINING

Speciality: 2314.01 – Petrochemicals

Field of science: Technical sciences

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Baku – 2024

The work was performed at the Institute of "OilGasScientificResearchProject" of the State Oil Company of the Respublic of Azerbaijan

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CHARACTERISTICS OF THE WORK

Relevance of the topic and the degree of elaboration. One of the important problems is the preparation of effective new compositions and the acquisition of reagents, the development of more promising technologies to eliminate complexities during oil refining. Currently, this problem remains relevant, despite the fact that there are various methods for eliminating existing complexities. The use of economically efficient, high-quality and universal reagents in industry in the preparation of oil produced in mines and at the next stage of processing at the plant is of great importance[1].

Since the reagents used in modern times are less efficient for the complete elimination of problems arising in the process of accumulation of salt deposits in the equipment during processing, on the other hand, the high cost of inhibitors purchased from foreign countries has made the development of new salt-making, corrosion inhibitors and deemulgators relevant[2].

Thus, the development of new reagents, compositions and technologies to eliminate complexities arising during the extraction and processing of oil is one of the problems that are always under control. Currently, the well-known means used for the prevention of the deposition process of salts, which have a difficult solubility, do not meet modern requirements. If we group and analyze the resulting salt deposits according to their chemical properties, we will see that the causes of their formation are different, just as all salts have different compositions. Therefore, one of the urgent problems is how important it is to scientifically investigate the process of salting and develop new inhibitors to eliminate the complexities created by them.

One of the main problems of the oil industry is that most of the extracted oil consists of a water-oil emulsion. The excess of water and mechanical mixtures in the composition of the emulsion creates many

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[1] Abbasov, V.M. Study of the effectiveness of a mild steel corrosion inhibitor in H_2S medium / V.M.Abbasov, N.I.Mursalov, D.B.Aghamaliyeva [et all] // Processes of petrochemistry and oil refining, – 2024. Vol.25, No.2, – pp. 366-375.

[2] Safarov, G.I. Oil and gas processing technology / Q.I.Safarov, A.S.No, no. - Baku: "Maarif", – 2000. - 464 P.

difficulties during transportation. And this leads to a high cost of oil. It is impossible to imagine their degradation without reagents, given that emulsions that cause complexations are more resistant. Therefore, the development of new technology using reagents of universal properties during the processing of continuous oil-water emulsions always retains its relevance. Due to the high cost of imported components for the preparation of new compositions for this purpose, the cost of applied reagents becomes high. Therefore, one of the latest achievements of the development of science – the transformation of nanoparticles and compositions based on them into the oil industry-became necessary. Currently, there is no field of activity in which nanotechnology would not be applied. The application of nanotechnology is considered more effective in the recent elimination of complexities in the oil refining process. Currently, the range of nanoscale reagents is growing more rapidly.

The development and study of more efficient nanocomposite deemulgators in the process of dehydration and desalination of oil emulsions is one of the urgent issues. The use of nanotechnology to eliminate complexities during oil refining can improve the quality of the prepared oil in accordance with the requirements for further transportation and processing.

Notice that, it is of great importance to develop completely new nanoscale compositions using low-cost and easy-to-use surface-active substances (SAS) and aluminum nanopowders.

Object and subject of the research. The development and study of nanoscale compositions based on quadruple amines, SAS and nanopowders was taken as the object of research. The subject of the study is the preparation of reagents with high deemulgating and inhibitory properties using nanoscale compositions.

Goals and objectives of the study. It is the development and application of stable and composite compositions of new universal properties in order to eliminate various kinds of complexities arising during oil refining. To solve the problem, the following issues have been resolved:

- obtaining and research of new base reagents based on quadruple amines;

- of various origins (carbonate, sulfate, etc.) development of stable reagents and nanocomposite inhibitors to prevent salt deposition;
- development of a new deemulgator for complex dehydration and desalination of oil;
- development of new nanodemulgators for complex dehydration and desalination of oil

Research methods. In the study of the structure and properties of the compositions developed in the dissertation work, modern methods of physico-chemical research were used. Infrared-spectra of the compositions and some quadruple organic amines were drawn on spectrometers Thetmoscientific, Nicoletis 10 and Bruker IFS-113V by preparing tablets in vaseline or fluorinated oil suspension, as well as KBr.

Kinematic, dynamic viscosities and densities of the prepared compositions were determined using the device "StabingerViscometer-SVM 3000" of the brand "Anton Paar" of the modern type. Also, using various physical research methods, the freezing temperature of the compositions, the pH-hydrogen indicator, the content of water in oil, mechanical mixtures and chloride salts and ions in the samples were determined.

The main provisions of the defense.

- inhibitors against salinity;
- nanocomposite inhibitors against salinity;
- deemulgator for complex dehydration and desalination of oil;
- nanodemulgators for complex dehydration and desalination of oil.

Scientific novelty of the research.

- Of various origins (carbonated, sulfate, etc.) reagents of fixed composition were synthesized to prevent the deposition of salts;
- Nanocomposite inhibitors have been developed to prevent the deposition of salts;
- Developed a new deemulgator for complex dehydration and desalination of oil;
- New nanodemulgators have been developed for complex dehydration and desalination of oil.

Theoretical and practical significance of the research.

After the application of the "NTK" brand deemulgator as a

nanoscale composition for the preparation of oil in the commodity tank park (CTP) of the "Neft Dashlari" Oil and Gas Production Department (OGPD), the oil was purified faster from liquid and mechanical mixtures, and the deemulgator consumption was less. Thus, the consumption rate of "Sarol" deemulgator for 1 ton of oil used before was 30 grams, while the consumption rate of "NTK" brand deemulgator for 1 ton of oil was 25 grams. Taking into account the fact that on average 3000 tons of oil are processed daily in "Neft Dashlari" OGPD, high economic benefits have been achieved.

After application of "NTK" brand deemulgator in wells no. 1302, 1309, 1284 with emulsion in Palchig Pilpilesi field of "Neft Dashlari" OGPD, as a result of decomposition of emulsion and better filtration of liquid, 240 tons of additional oil was produced.

The quality indicators of the oil prepared as a result of the application of nanodeemulgator of "NTK" brand in mining conditions developed on the basis of SAS, solvents and nanopowders for dehydration, desalination operations of oil emulsion corresponded to the requirements of AZS 115-2004 and was evaluated as group I oil.

Acts on the application of the newly developed nanocomposition are attached to the dissertation.

"Method of obtaining mineral salt-rubble inhibitor" is protected by the patent of the Republic of Azerbaijan no. I 2022 0038.

Approbation and application.

The main results of the dissertation are reflected in 21 scientific publications. 10 of them are articles, 10 are conference materials and theses, and 1 is a patent of the Republic of Azerbaijan.

Materials of the dissertation were reported and discussed: Akdeniz international multidisciplinary work Congress, (Mersin, Turkey, March 1-3, 2019); Readings of A.I.Bulatov, Materials of III International scientific and practical conference, (Crasnodar, Russia, on March 31, 2019); Readings of A.I. Bulatov, Materials of IV International scientific and practical conference, (Crasnodar, Russia, on March 31, 2020); International Conference on Actual Problems of Chemical Engineering, (APCE-2020, Baku, Azerbaijan, december 24-25, 2020); III international scientific conferences of students and young researchers dedicated to the 99th anniversary of national leader

Heydar Aliyev, (April 18-29, 2022, Baku, Azerbaijan); Republican Scientific Conference of doctoral, masters and young researchers on “chemistry and Chemical Technology” dedicated to the 99th anniversary of national leader Heydar Aliyev, (Baku, Azerbaijan, may 18-19, 2022); Readings of A.I. Bulatov, Materials of VII International scientific and practical conference, (Crasnodar, Russia, on March 31, 2023); International scientific-practical conference on “Heydar Aliyev and Azerbaijan oil strategy: advances in oil and gas geology and geotechnologies” dedicated to the 100th anniversary of the National Leader of the Azerbaijani people Heydar Aliyev, (Baku, Azerbaijan, May 23-26, 2023); Republican scientific conference on “modern approaches in Chemistry and Chemical Technology” (Baku, Azerbaijan, December 14, 2023).

The organization where the dissertation work was performed. The presented dissertation was performed at SOCAR's "OilGasGcientificResearchProject" Institute.

Author's personal participation. The author personally took part in the implementation of the dissertation, in the planning of the work, in the collection of literature materials, in the writing of the main experimental studies, including articles, theses and dissertations.

The scope and structure of the work. The dissertation consists of an introduction, 3 chapters, a list of literature in 141 titles and 2 appendices. The work is expressed on 151 pages, there are 23 tables, 43 pictures, 2 schemes. The dissertation work consists of a total of 192300 marks (introduction 10949, chapter I 61644, chapter II 105040, chapter III 11937 and conclusion 2768 marks), excluding tables, pictures and a list of literature.

In the **introductory** part of the dissertation, the relevance of the research carried out on the topic is substantiated, the scientific innovations of the work, the main provisions for defense and methods for solving the problems posed are commented on.

In the first chapter, scientific works published in the last 10-15 years in the Republic, near and far abroad on the causes of the formation of complexities during oil refining, methods of combating them, solution of existing problems are commented. Information on the causes of salinity during processing and deemulsation of water-oil

emulsions has been widely studied. The information on the composition of new reagents and compositions developed to prevent salinization and decomposition of water-oil emulsions, the technology of their production, the mechanism of their action is given.

The second chapter is devoted to the development and preparation of new reagents and nanocompositions against complexations during oil refining, determination of their physico-chemical properties, study of the dynamics of the effect of the obtained reagents against salt deposits in a comparative way, laboratory test results.

The third chapter provides the results of mining tests of the developed new nanocomposition.

After the introduction of the “NTK” brand deemulgator for the preparation of oil in the CTP of the OGPD “Neft Dashlari", the oil was cleaned faster from liquid and mechanical mixtures, and the deemulgator consumption was less. Thus, the norm of consumption of “Sarol” deemulgator for 1 ton of oil used before was 30 g, and the norm of consumption of “NTK” brand deemulgator for 1 ton of oil was 25 g. Taking into account the fact that on average 3000 tons of oil are processed daily in the OGPD “Neft Dashlari", it will be felt that high economic benefits have been achieved.

After application of “NTK” brand deemulgator in wells no. 1302, 1309, 1284 with emulsion in Palchig Pilpilesi field of “Neft Dashlari" OGPD, as a result of dispersion of emulsion and better filtration of liquid, 240 tons of additional oil was produced.

The tests were positively evaluated and the oil developed using the new technology fully met the requirements of AZS 115-2004.

The completed dissertation work concludes with conclusions, a list of cited sources of literature and appendices.

THE MAIN CONTENT OF THE WORK

Acquisition and research of compositional deemulgators

It was used in the formulation of Laprol 4202 - 2B-30 (ТУ 2226-039-05766801-2000) as a block joint polymer based on ethylene-and propylene oxides for deep dehydration and desalination of water-oil emulsions. Many solvents were used as a solvent of laprol, but more effective result was obtained when using methanol (ГОСТ 2222-95) or isopropyl alcohol (ГОСТ 9805-84).

Laprol 4202-2B-30 as SAS for the deemulsation of water-oil emulsions, methyl or isopropyl alcohol as a solvent and a substance with the addition of pentaethylenhexamine up to 2 % of the total mass was conventionally called pentaethylenaminlaprol (PENAL).

The density of the PENAL deemulgator at 20 °C was 0,9311 g/cm^3, the kinematic viscosity was 22,663 mm^2/s, the dynamic viscosity was 21,102 mPa·s, the freezing temperature was below minus 15 °C, the hydrogen indicator was 10,4. The deemulgator is a clear colored liquid.

During the deemulsation of oil, reagents were obtained that have the property of more effectively decomposing and desalinating the oil emulsion. In the preparation of the new effective composition, non-ionogenic type Laprol 4202-2B-30, aluminum nanopowder, quadruple organic amine complex salts of mineral acids were used as additives. In this case, preference was given to oil-soluble reagents. Thus, by adding aluminum nanopowder (L-ALEX 90-110 nm) (ТУ-1791-003-36280340-2008) to the base deemulgator PENAL deemulgator 0,005 % (mass), the newly developed composition was conventionally called the nanoscale composition - “NTK”.

The density of the NTK composition at 20 °C was 0,9245 g/cm^3, the kinematic viscosity was 20,545 mm^2/s, the dynamic viscosity was 18,993 mPa·s, the freezing temperature was below minus 13 °C, the hydrogen indicator was 10,4. The composition is a transparent colored liquid.

Methods for obtaining a mineral salt deposition inhibitor

The method of obtaining inhibitors of mineral salt deposits was

based on the interaction of 85 % of organic amines of various classes with orthophosphate acid. Orthophosphate acid corresponding to ГОСТ 6552-80 was used in the synthesis.

Mono-, di-, tri-ethanolamines, ethylenediamine and tetra-methylethylenediamine were used as nitrogen-containing compounds in the synthesis.

Many salts of orthophosphate acid are used in the oil industry for various purposes. The new composition proposed by us for solving the existing problem belongs to the quadruple amine complex salts formed by organic amines with orthophosphate acid. Reagents of this type can be used as an inhibitor for the protection of water circulation systems of enterprises, oilfield equipment and transport pipes from mineral deposits, corrosion and biological damage.

What distinguishes this inhibitor from other analogues is the development of its synthesis by waste-free method without the use of additional toxic substances and the simpler way of obtaining the intended product.

The method of obtaining a mineral salt deposition inhibitor operating in mineralized environments consists in the interaction of nitrogen-containing organic compounds with 85 % orthophosphate acid. The intake of the proposed new inhibitor is carried out in two stages. As a nitrogen-containing organic compound, ethylenediamine is used at the beginning of the synthesis, and dihydro -, monohydro- and phosphate derivatives of ethylenediamine are used at the later stages. The interaction of ethylenediamine and its phosphate derivatives with orthophosphate acid is carried out at a temperature of 40 - 45 ºC in a ratio of 85 % orthophosphate acid equal to 1:1 mol. Then the obtained reaction products are cooled to 20 ºC and diluted with water until 10 % solutions are formed. Based on ethylenediamine and orthophosphate acid, ethylenediamine dihydrophosphate (EnDHF) (BR-4), ethylenediamine dihydrodiphosphate (EnDHDF) (BR-7), bisethylenediamine monohydrophosphate (BEnMHF) (BR-5), bisethylenediamine monhydrodiphosphate (BEnMHDF) (BR-8), trisethylendiamine phosphate (TenF) (BR-6) and salinity inhibitors containing trisethylendiamine diphosphate (TenDF) (BR-9) have been obtained.

Model mineral water samples prepared in a known way were used to carry out laboratory tests of the effect of the action of salt deposition inhibitors. In all sections of the dissertation, the determination of the defense effect of nanoscale, non-nanoparticles added and other compositions as inhibitors is given in the form of tables.

Tests of the protection effect of the developed inhibitors were carried out according to the methods known in the literature on the model of formation waters for the prevention of sulfated and carbonated salt deposits.

For $CaSO_4$		For $CaCO_3$	
$CaCl_2$	13,6 g/dm^3	$CaCl_2$	2,92 g/dm^3
$MgCl_2 \cdot 6H_2O$	1,24 g/dm^3	$MgCl_2 \cdot 6H_2O$	4,26 g/dm^3
Na_2SO_4	13,0 g/dm^3	Na_2SO_4	2,4 g/dm^3
NaCl	18,8 g/dm^3	NaCl	40,6 g/dm^3

Complex salt containing BR-7 prevents the formation of carbonate deposits in a carbonated solution with a consumption of 20-30 mg/l from 73,4 % to 90,9 %. BR-7 reagent is prevented from forming carbonate deposits at 20 mg/l consumption by 73,4 %, at 25 mg/l consumption by 87,6 % and at 30 mg/l consumption by 90,9 %. However, the effect of the BR-7 reagent against the formation of sulfate salts is at least slightly lower. So, between the consumption of 20-30 mg/l, the effect varies in the interval of 70,3-89,3 %.

BR-8 reagent prevents the formation of carbonate deposits in carbonated solutions at a consumption of 20-30 mg/l at a rate of 78,5-93,3 %, while the formation of sulfate salts at the same consumption of 76,5-90,6 %.

It should also be noted that the properties of the BR-9 complex reagent as a salinity inhibitor for carbonated and sulphated solutions are at least partially stronger than both analogues previously analyzed. Thus, the effect of BR-9 reagent against the formation of deposits of both carbonate and sulfate salts between 20-30 mg/l consumption is 82,4-94,8 and 79,8-92,9 %, respectively.

The reason that BR-9 reagent has a stronger property as a salt-forming inhibitor than its other two counterparts is due to the fact that the intramolecular hydrogen bond of the complex salt is broken in an

alkaline environment and the hydrolysis process is complete in stages.

When taking more than 30 mg/l of the mentioned three quadruple organic amine complex reagent, there is an increase in the effect of the action on the properties of the reagents as a salinity inhibitor. Comparing the salinity inhibitor properties of newly synthesized BR-4, BR-5, BR-6, BR-7, BR-8 and BR-9 reagents on the basis of ethylenediamine and orthophosphate acid among themselves and with the test results of known reagents, it is clear that BR-9 reagent produces a high protection effect in sulfated and carbonated water solutions with a consumption of 20; 25; 30.

It is known that in laboratory experiments with the consumption of the inhibitor in the amount of 5-30 mg/l, it is possible to recommend experimental-industrial tests of the inhibitor if its defense effect is 75-90 %.

Salinity inhibitor compositions based on ethylenediamine, quadruple amines of orthophosphate acid and hydrochloric acid the complex quadruple

Organic amines formed by organic amines with orthophosphate and hydrochloric acid form organic bases and corresponding acids during hydrolysis. Taking into account the chemical reactions that occur during the interaction of hydrolysis products with aluminum nanoparticles, it is possible to obtain a composition of a more effective nature.

As an amine-containing organic compound, EnDHF (BR-4), BEnMHF (BR-5) and TenF (BR-6) are obtained, which are quadruple amine derivatives with orthophosphate acid of ethylenediamine in the first place, and are used as an initial substance in synthesis. Then, on their basis, quadruple amine complex salts containing EnDHDF (BR-7), BEnMHDF (BR-8) and TenDF (BR-9) were obtained and studied. The interaction of reagents-EnDHF, BEnMHF, TEnF and 21 % hydrochloric acid is carried out in a ratio of 1:1; 1:2 and 1:3 stoichiometric moles at a temperature of 35-40 °C, then the obtained ethylenediamine orthophosphate and hydrochloric acid mixtures are cooled to 20 °C and diluted with water until a 10 % solution is obtained. The obtained compositions were encrypted as KBR-7, KBR-

8 and KBR-9, respectively.

According to the methodology of the tests, the samples are kept in the thermostat at 80 ^{o}C for 5 hours after adding the inhibitor to both the non-inhibitor and the layer water model. After a certain time, the sediment was filtered from the cooled samples and the residual amount of calcium cations in it was determined by trilonometric titration.

As a continuation of the research work on more efficient new Salt-forming inhibitors, at this stage, laboratory tests of the components of inhibited hydrochloric acid and ethylenediamine with orthophosphate acid in various mole ratios of EnDHF monochloride, BEnMHF dichloride and TEnF trichloride (KBR-7, KBR-8, KBR-9), prepared on the basis of synergistic mixtures, were carried out as a It should be noted that the properties of KBR-7, KBR-8 and KBR-9 reagents as a salinity inhibitor in model formation waters with a consumption of 20-30 mg/l were studied and the results obtained were analyzed comparatively. These reagents show greater efficiency in both sulfated and carbonated solution as a salinity inhibitor. In view of this effect, compositions with the addition of aluminum nanoparticles based on BR-7, BR-8 and BR-9 reagents were developed and studied to further enhance synergism. In laboratory tests, the compositions EnDHF monochloride, BEnMHF dichloride, and TEnF trichloride were used in 10 % aqueous solutions at a consumption of 20; 25 and 30 mg/l.

Newly developed compositions significantly prevent the formation of “carbonated” and “sulfated” salt deposits, depending on consumption, and the inhibitory effect of all three compositions on carbonate deposits is higher. Comparing the properties of the compositions as salt-forming inhibitors among themselves, it is observed that the inhibitory properties of KBR-7 < KBR-8 < KBR-9 are enhanced. All three inhibitors show a stronger defense effect at a consumption of 30 mg/l against carbonated and sulfated salt deposits. For example, the composition of EnDHF monochloride at a consumption of 30 mg/l prevents the formation of sulfated sediments by 89,3 %, and carbonate sediments by 90,2 %. The other two compounds - BEnMHF dichloride and TenF trichloride-prevent the deposition of sulfated sediments by 91,4 % and 92,9 %, respectively,

while carbonate salts are capable of preventing the deposition of 93,3 % and 94,4 %. It should be noted that to prevent the formation of carbonate salts, only the consumption of inhibited hydrochloric acid is required at 300 g/t. And this is not profitable both economically and from the point of view of corrosion.

The results of laboratory tests of synthesized quadruple Amine BR-4 - BR-9 salinity inhibitors were noted to be weaker than the results of KBR-7 - KBR-9 compositional salinity inhibitors developed on the basis of the mentioned reagents. Therefore, taking into account the positive results of KBR-7 - KBR-9 salinity inhibitors, preference was given to the development and research of new nanoscale composition salinity inhibitors based on BR-4 - BR-9 reagent.

Composition desalination inhibitors based on BR-7, BR-8, BR-9 reagents and nanoparticles

As an amine-containing compound, quaternary ammonium salts are meant, which are formed by orthophosphate acid in different mole ratios of ethylenediamine, which is generalized separately under the name BR-7, BR-8 and BR-9 reagents. Obtaining new nanoscale compositions is carried out at a temperature of 35-40 °C, at different stoichiometric mole ratios of reagents and by adding nanoparticles. After that, the separately obtained quadruple ammonium salts are cooled to 20 °C and diluted with water until a 10 % solution is obtained from them. Aluminum nanoparticles were added to the obtained 10 % solutions at the rate of 0,005 %. The base reagents with the addition of aluminum nanoparticles were adopted to be referred to as NKBR-7, NKBR-8 and NKBR-9, respectively.

It should be noted that the aluminum nanoparticle was added to the base reagents BR-7, BR-8 and BR-9 in the formulation in the amount of 0,0001-0,005 %, the positive effect was observed only when adding in the amount of 0,005 %.

In the dissertation work, aluminum, iron and copper nanoparticle additives were used as surface forming reagents. But in all cases, inhibitors with the addition of aluminum nanoparticles showed a high result.

The density of the obtained compositions at 20 °C is

1050-1100 kg/m^3, the kinematic viscosity is 30-40 mm^2/s, the freezing temperature is minus 6-10 °C the hydrogen indicator varies in the range of 5,5-7,5. They are transparent liquids, the color of the compositions of which varies from light to weak yellow

When adding to sulfate and carbonated water solutions with a consumption of 20; 25; 30 mg/l of newly synthesized salinity inhibitors, a minimum protection effect of 83,7-86,8 % is created, respectively. The maximum protection effect is observed when adding the inhibitor to sulfate and carbonated solutions with a consumption of 30 mg/l with the addition of bisethylenediammonium monohydrodiphosphate compound nanoparticle. In this case, the maximum protection effect of the inhibitor is 96,2 % for sulfated solutions and 98,4 % for carbonated solutions.

When the prepared composites are added to aqueous solutions containing calcium carbonate and calcium sulfate with a consumption of 30 mg/l, the inhibitor has a higher protection effect compared to cases with a consumption of 20; 25 mg/l.

Less or more than a certain amount of a quadruple amine complex compound in the composition of the compositions leads to a weakening of the corresponding properties of salinity inhibitors. The weakening of the inhibitory property of a quadruple amine complex compound when its content is too high can be explained by their inability to mate with waters with high minerality.

Nanoscale salinity inhibitors based on amine alcohols and quadruple amines of orthophosphate acid

Mono -, di - and tri - ethanolamines and mono -, di-and tri-ethanolammonium phosphates based on orthophosphate acid have been developed. The mineral salt precipitate inhibitor proceeds according to a one-stage reaction scheme, and the obtained chemical compounds are thinned with water. In the process of obtaining mineral salt sediment inhibitors, a useless extraneous substance is not formed, and therefore environmental pollution does not occur. To obtain salinity inhibitors, appropriate organic amines in the amount of 1-3 moles are separately added to a three-throat flask equipped with a mechanical mixer, a reverse coolant, a thermometer and a separating

flask. The reaction mixtures are heated to 60-65 ºC, the mechanical mixer is turned on and, by means of a separating funnel, orthophosphate acid in an amount of 1 mole is added to the reaction mixtures by dropper. After the complete addition of a certain amount of orthophosphate acid taken according to the calculation to the reaction mixtures, the reaction is stirred for another 2 hours at the specified temperature. Reaction products-ammonium phosphates are cooled to 20-25 ºC, aluminum nanoparticles are added and thinned until 2 % solutions are obtained.

Synthesized mono -, di-and tri-ethanol ammonium phosphates are clear liquids that change from light-yellow to dark-yellow depending on the increased stoichiometric ratio and are named as the respective BR-1, BR-2 and BR-3 base reagents. The base reagents with the addition of aluminum nanoparticles were adopted to be referred to as NKBR-1, NKBR-2 and NKBR-3, respectively.

BR-1 - BR-3 base reagents show inhibitory properties in the formulation of 66,3-79,4 %, depending on the composition and quantity. The protection effect of NKBR -1 - NKBR-3 compositions with inhibitory properties is 70,2-97,4 %, respectively. When increasing the amount of the nanoscale composition inhibitor from 20 mg/l to 30 mg/l, a dynamic increase in the effectiveness of the inhibitor is observed, and the maximum result is achieved in the amount of 30 mg/l. According to the given data, it can be said that as the amount of nanoscale composition increases, the effectiveness of salinization prevention is optimized more rapidly. On the other hand, when following mono -, di - and tri - ethanolamine sequences, the number of alcohol hydroxyl groups increases, there is a partial change in the effectiveness of the composition (82,8 < 91,9 < 97,4).

Salting inhibitors based on tetramethylethylenediamine orthophosphate and nanoparticles

Tetramethylethylenediamine was used as an amine-containing organic compound at the initial stage in the preparation of a new salt-forming inhibitor. At the next stage, as a result of its interaction with nanoparticles in different mole ratios, a nanocomposition was obtained. The composition of the inhibitory composition includes such

components as the quadruple Amine complex salt of orthophosphate acid of the brand “KT” and tetramethylethylenediamine of the company “Reanol”, aluminum nanoparticle with a size of 90-110 nm.

Interaction of orthophosphate acid with tetramethyl-ethylenediamine at a temperature of 40-45 ^{o}C, as a result of the interaction of reagents in the proportions of 1:1; 1:2 and 1:3 mol, respectively, salts containing H_2PO_4 tetramethylethylene-diammonium-dihydrophosphate (HTETMEN) (BR-10), HPO_4 $(HTETMEN)_2$ (BR-11) and PO_4 $(HTETMEN)_3$ (BR-12) with the general formula are formed. At the same time, tetramethylethylenediammonium compounds of orthophosphatic acid are formed in the form of syrups. After that, the syrup-shaped salts, which have a yellowish white color, are cooled to 20 ^{o}C and 10 % aqueous solutions are prepared separately from them. With intensive mixing, aluminum nanoparticles are added to each of the finished solutions in the amount of 0,0001-0,005 % of the total mass.

When adding the base reagent to sulfate and carbonated water solutions with a consumption of 20; 25; 30 mg/l, a protection effect of more than 80 % is created. The effectiveness of the inhibitor in all cases depends on its chemical composition, consumption, nature of salts deposited in rocks and other factors. Comparing the properties of BR-10, BR-11 and BR-12 reagents as a salinity inhibitor, it seems that the BR-11 inhibitor in an amount of 30 mg/l prevents the deposition of 85,5 % sulfates and 89,3 % carbonates. When adding the inhibitor to sulfate and carbonated water solutions with a consumption of 30 mg/l, the maximum protection effect is observed.

Nanocomposites NKBR-10, NKBR-11, NKBR-12 were developed with the addition of aluminum nanoparticles that make up a percentage of 0,0001; 0,001 and 0,005 % of the total mass to the base inhibitor. The nanocomposite NKBR-11, which contains 0,005 % of the total mass as a nanoparticle, shows maximum efficiency. NKBR-11 nanocomposite in a mass amount of 30 mg/l prevents the maximum deposition of 95,2 % sulfates and 97, 5 % carbonates.

In order to inhibit the process of accumulation and growth of salt crystals, salinity inhibitors create mutual communication with the crystals of salts. This communication helps to keep the crystal-forming

cations and anions suspended during the process of their movement in solution. The mechanism of action of nanocomposition, which is a salinity inhibitor, consists in the adsorption of molecules in salt crystals, which complicates their aggregation and aggregation ability.

Representatives of nanoscale inhibitors form a protective layer on the surface of salt “embryos”, preventing their growth and not allowing crystals to accumulate on the surface of protected equipment, merging among themselves over time. On the other hand, it has been established that inhibitors show the highest defense effect with the "barrier effect". Various types of amines used in the dissertation work are included in inhibitors as complex-inducing reagents and together with cations of alkali-earth metals form water-soluble anion or helate-type complexes, preventing their deposition in the system.

Development and research of new salinity inhibitors based on NKBR composition and SAS

Compositions based on newly obtained quadruple amine base reagents, surfactants and aluminum nanoparticle have also been developed and studied as salt inhibitors.

The modern and current trend of eliminating the problem of salting is based on the preparation of “compostable” salting inhibitors, including the main reagents and additives.

The aluminum nanoparticle produces a “small impact and excitation effect". When introducing non-ionogenic SAS into the solvent, the cost of surface tension at the border decreases. The compositions are adsorbed in salt deposits and contribute to a decrease in the cost of surface tension at the border with the solvent. As a result of this, the effectiveness of solubility and the dissolution of salt deposits occur. For this reason, salting is prevented.

For the removal of salt deposits, new compositions of the NKBRSAM series have been developed on the basis of various compositions BR and NKBR, dispersant of the ES 9660A brand, Laprol of the 4202-2B-30 brand and water. The interaction of reagents is carried out at a temperature of 45-50 ^{o}C.

The density of the prepared compositions at 20 ^{o}C is 1020-1050 kg/m^3, the kinematic viscosity is 25-35 mm^2/s, the freezing

temperature is minus 5-15 °C, the hydrogen indicator varies in the range of 3-7,5. The compositions are transparent liquids of yellowish-brown color.

Depending on the content of inhibitors and model waters, the protection effect at a consumption of 30 mg/l of the reagent was 82,7 % minimum for sulfated solutions and 96,5 % maximum. For carbonated solutions, the protection effect was determined to be a minimum of 86,4 % and a maximum of 98,8 %.

Test results of samples containing NKBRSAM-3, NKBRSAM-8 and NKBRSAM-11 show that they produce a higher protection effect. A distinctive feature of these compositions is that organic amines have a stronger helate effect, and the amount of laprol and dispersant is less than that of SAS, which is part of other compositions. It has been established that samples of salinity inhibitor containing non-ionogenic SAS with a percentage of 8 % show stronger inhibitory properties.

The results of determining the defense effect of the developed NKBRSAM-3 salinity inhibitor are reflected in the figure below.

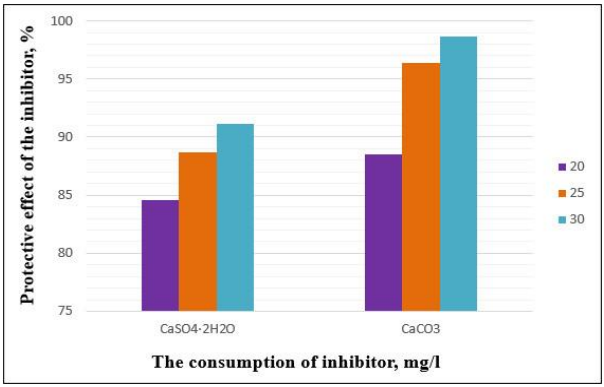

Figure. Protection effect of NKBRSAM - 3 salt inhibitor dependence of the inhibitor on its consumption

Development of nanocompositions based on the theory of the effect of “small impact and excitation"

0,001; 0,005; 0,01; 0,07 and 0,1 % iron (Fe 50-70 nm) or aluminum nanoparticles (L-ALEX 90-110 nm), as well as 0,05 %

carboxymethylcellulose (CMC) were added to the chemically treated water used in the treated water lines and equipment during oil refining and physico-chemical analyzes of these water samples were carried out. By adding metal nanoparticles and CMC to chemically treated water on the basis of "small impact and excitement" effect, the overall roughness, alkalinity, chlorine ion content, hydrogen indicator decreased to the required norm. As a result of the research, when adding aluminum nanoparticles and CMC to water, alkalinity decreased from 2,1 mg-ekv/l to 0,2 mg-ekv/l, chlorine ion content decreased from 1,42 mg-ekv/l to 0,09 mg-ekv/l, pH from 8,9 to 7, overall roughness from 0,058 mg-ekv/l to 0,008 mg-ekv/l. Studies have shown that 0,005 % of the nanoparticles used are more optimal.

Testing of the selected new nanoscale composition in laboratory conditions and analysis of its results

Laboratory tests of the processed compositions were carried out with emulsified oil of Baku Oil Refinery (BOR) named after Heydar Aliyev and "Neft Dashlari" OGPD. Under temperature conditions of 20 ^{o}C, the density of oil was 0,85 g/cm^3, the residual water content in the oil was 0,2 %, the content of chloride salts was 29,24 mg/l. To prepare the emulsion, 10 % of the oil sample is supplied with fresh water and mixed continuously at a temperature of 70 ^{o}C. Then reagents at a dose of 45 g/t are added to it in accordance with the norm adopted in BOR and kept in a thermostat at a temperature of 70 ^{o}C for 4 hours. After the studies were completed, the samples were cooled to 20 ^{o}C. At the next stage, the amount of residual water in the oil was determined according to the methodology specified in ГОСТ 14870-77, the amount of chloride salts in ГОСТ 21534-76. Tests of the new deemulgator compositions by known methods in laboratory conditions were carried out in comparison with the base reagents used in BOR. At the end, the amount of residual water in the oil was determined by The Dina-Stark method.

During the deemulsation of oil with the application of new reagents in the implementation of the tests, there was a violation of its stability, a change in its quality, an acceleration of the separation of the emulsion into the initial phases. The results of the laboratory tests

carried out are presented in table 1.

Table 1.

Determination of chloride salts in oil samples taken from BOR named after H.Aliyev

Name of the deemulgator	The amount of reagent, g/t	Normal condition	The amount of chloride salts, mg/l
-	-	Unprocessed	29,23
Reagent-free	-	Unwashed, deemulsated	26,4
Base deemulgator 50 %	45	Unwashed, deemulsated	20,46
PENAL 50 %	45	Unwashed, deemulsated	15,5
Base deemulgator	45	Unwashed, deemulsated	17,4
PENAL	45	Unwashed, deemulsated	13,8
Reagent-free	-	Washed, deemulsated	24,2
Base deemulgator	45	Washed, deemulsated	7,01
PENAL	45	Washed, deemulsated	4,16
Base deemulgator 50 %	45	Washed, deemulsated	15,19
PENAL 50 %	45	Washed, deemulsated	12,31

The nanoscale compositions NKBR-3, NKBR-8, NKBR-11 were separately added to the PENAL base reagent to 1-5 % of the total mass and their deemulsation properties were studied. The newly developed compositions were conventionally named as PNTK-3, PNTK-8 and PNTK-11, respectively. Analysis of the results of the research shows that the new nanocomposition obtained when adding a maximum of 0,005 % nanocomposite to the PENAL base reagent shows higher efficiency in deep dehydration and desalination of oil emulsions. The research work was analyzed in comparison with the results obtained from the study of the base deemulgator applied in BOR both without additives and in the form of a 50 % solution. After

deemulsion, the residual water content in the oil samples was minimal.

The newly developed penal and NTK, PNTK-3, PNTK-8, PNTK-11 compositions showed a higher deemulsation effect during the process of desalination and deemulsation of oil, compared with the base deemulsator. The content of chloride salts in oil has decreased to minimal limits. The results of the study are presented in table 2.

Table 2.

Results of laboratory tests of PENAL, NTK, PNTK-3, PNTK-8 and PNTK-11 compositions

Deemulgator name	Tempe-rature, ^{o}C	Amount of reagent, g/t	The amount of chloride salts, mg/l	Amount of residual water, %
Primary crude oil	70	-	29,23	0,2
Reagent free deemulsion	70	-	24,2	0,18
PENAL	70	45	4,16	0,039
NTK	70	45	3,06	0,031
PNTK-3	70	45	3,30	0,035
PNTK-8	70	45	3,51	0,038
PNTK-11	70	45	3,42	0,036

As can be seen from the table, compositions with the addition of nanoparticles deeper dehydrate and desalinate the oil emulsion. After processing the oil emulsion with nanoparticle composition, the separated water was analyzed. The results of water analysis have shown that after processing, its softness increases significantly and becomes environmentally friendly for further use.

Application of a new nanoscale composition in production against complexities during oil refining

Mining tests of “NTK” brand deemulgator were carried out during the preparation of oil in the CTP of the “Neft Dashlari” OGPD and in wells no. 1302, 1309, 1284 with emulsion products in Palchig Pilpilesi field of “Neft Dashlari" OGPD.

As a result of testing at CTP, the oil was purified faster than liquid and mechanical mixtures, and the deemulgator consumption was lower. Thus, the norm of consumption of “Sarol” deemulgator for 1 ton of oil used before was 30 grams [the price of one ton of deemulgator is 4603 Azerbaijani manat (Azn)], and the norm of

consumption of “NTK” brand deemulgator for 1 ton of oil was 25 grams (the price of one ton of deemulgator is 3750 Azn). Taking into account the fact that on average 3000 tons of oil are processed daily in the OGPD “Neft Dashlari", it will be felt that high economic benefits have been achieved. 8 hours after the completion of the test work, the oil analysis showed that the amount of residual water in the oil was 0,03 %.

After application of “NTK” brand deemulgator in wells no. 1302, 1309, 1284 with emulsion in Palchig Pilpilesi field of “Neft Dashlari” OGPD, as a result of dispersion of emulsion and better filtration of liquid, 240 tons of additional oil was produced. Economic benefits amounted to 60 thousand Azn.

It can be seen from the mentioned results that the oil treated with “NTK” reagent was assessed as group I oil, fully meeting the requirements of AZS 115-2004. The deemulsation feature of the “NTK" brand deemulgator was positively assessed. The results are reflected in the acts drawn up.

CONCLUSIONS

1. New nanocomposition inhibitors have been developed to prevent salt deposits of various origins (calcium, magnesium carbonate and sulphate) during oil refining:

   - when increasing the amount of NKBR series nanocompositions prepared by adding aluminum nanopowder to mono -, di- and tri-ethanolammonium phosphates from 20 mg/l to 30 mg/l, the defense effect for carbonated and sulfate solutions is from 70,2 % to 97,4 %, respectively [11, 20];

   -the maximum protection effect of NKBR-8 nanocomposite 30 mg/l of bisethylenediammonium monohydrodiphosphate-containing inhibitor co-developed with aluminum nanopowder is 96.2 % and 98.4 % for sulfated and carbonated solutions, respectively [6, 8, 10];

   - nanocomposite NKBR-11, co-developed with aluminum nanopowder of bistetramethylethylenediammonium monohyd-rophosphate salt, prevents the deposition of sulfates in the amount of 30 mg/l by 95,2 % and carbonates by 97,5 % [17];

-it has been established that the new NKBRSAM-8 reagent based on BR and NKBR, ES 9660A dispersant, 4202-2B-30 brand Laprol and water with different composition has a protection effect of 30 mg/l at a maximum of 96,5 % for sulfated solutions and 98,8 % for carbonated solutions [12, 14, 18, 21].

2. The prepared TenF trichloride-containing inhibitor prevents the deposition of sulfated salts by 92,9 %, while it prevents the deposition of carbonated salts by 94,4 % [7].
3. By adding aluminum nanoparticles and CMC to chemically treated water on the basis of “small impact and excitation effect", alkalinity decreased from 2,1 mg-ekv/l to 0,2 mg-ekv/l, chlorine ion content decreased from 1,42 mg-ekv/l to 0,09 mg-ekv/l, pH from 8,9 to 7, total roughness from 0,058 mg-ekv/l to 0,008 mg-ekv/l [4, 9, 13].
4. When using 45 g/t from the PENAL deemulgator designed for dehydration and desalination of oil, the amount of chloride salts was 4,16 mg/l, and the amount of residual water was 0,039 % [1, 2].
5. As a result of the introduction of the newly developed composition of the brand “NTK", the content of residual water and chloride salts in the oil fully meets the requirements of AZS 115-2004. When subjected to oil samples for deep dehydration and oil desalination by nanocomposition “NTK", the amount of chloride salts is 3,06 mg/l, and the amount of residual water is 0,031 % [3, 5, 19].
6. After using the “NTK" brand deemulgator for the preparation of oil in the CTP of the OGPD, the oil was cleaned of liquid and mechanical impurities faster, and the consumption of the deemulgator was less. Thus, the consumption rate of the "Sarol" deemulgator for 1 ton of oil used earlier was 30 grams, and the consumption rate of the "NTK" brand deemulgator for 1 ton of oil was 25 grams. Taking into account the fact that the OGPD “Neft Dashlari" processes an average of 3000 tons of oil daily, it will be felt that high economic benefits have been achieved.
7. After the application of “NTK” brand deemulgator with emulsion in wells no. 1302, 1309, 1284 in Palchig Pilpilesi field of “Neft Dashlari" OGPD, as a result of dispersion of emulsion and better filtration of liquid, additional 240 tons of oil were produced.

THE MAIN RESULTS OF THE DISSERTATION WORK WERE PUBLISHED IN THE FOLLOWING ARTICLES AND THESES:

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The defense will be held on 27 December 2024 at 14^{00} at the meeting of the Dissertation council ED 1.17 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at Institute of Petrochemical Processes named after academician Y.H.Mammadaliyev of Republic of Azerbaijan Ministry of Science and Eduction

Adress: Khojali ave., 30, AZ-1025, Baku, Azerbaijan

Dissertation is accessible at the Library of Institute of Petrochemical Processes named after academician Y.H.Mammadaliyev.

Electronic version of the abstract is available on the official website www.nkpi.az of the Institute of Petrochemical Processes named after academician Y.H.Mammadaliyev.

Abstract was sent to the required addresses on 26 November 2024.

Signed for print: 15.11.2024

Paper format: A5

Volume: 38315

Number of hard copies: 20