ABSTRACT

of the dissertation submitted for the degree of Doctor of Philosophy (PhD)

in the specialty 6D073900 – Petrochemistry

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DEVELOPMENT AND APPLICATION OF COMPOSITE REAGENTS FOR THE BREAKING OF WATER–OIL EMULSIONS AND THE TREATMENT OF PRODUCED WATER FOR REUSE IN TECHNOLOGICAL PROCESSES

Relevance of the research topic. The current state of the oil production industry in the Republic of Kazakhstan is characterized by the transition of most major oil fields (Uzen, Botakhan, Karazhanbas, etc.) to the late stage of development. This stage is accompanied by a progressive increase in water cut (up to 80–90%), leading to the formation of highly stable water-in-oil emulsions.

The scientific and practical relevance of the study is determined by the following factors:

- complex composition of crude oil: The presence of significant concentrations of asphaltenes, resins, and paraffins in the oils of Western Kazakhstan, combined with the ultra-high mineralization of formation waters (up to 320 g/L), leads to the formation of highly resistant interfacial films at the oil–water interface. This significantly reduces the efficiency of conventional industrial demulsifiers and necessitates the use of excessively high reagent dosages and elevated temperatures for emulsion treatment.

- energy efficiency and environmental considerations: In the context of the global trend toward reducing carbon footprint and energy consumption, the development of demulsifiers capable of operating without thermal treatment is of critical importance. This approach enables a substantial reduction in the energy required for heating well fluids and decreases emissions associated with fuel combustion.

- closed-loop water management: The efficiency of oil treatment is directly correlated with the quality of produced water. Given the increasing scarcity of water resources, the development of advanced treatment methods for formation water reuse, particularly for reinjection into the reservoir (pressure maintenance systems), represents a strategic objective for sustainable resource management in the oil industry.

Thus, the development of scientifically grounded composite reagents and innovative methods for the reagent-based post-treatment of produced water using

activated aluminum alloys represents a relevant scientific and technical challenge, the solution of which is of significant importance for the oil and gas sector of the Republic of Kazakhstan.

Research objective:

To provide a scientific rationale and experimental validation for the development of highly efficient composite demulsifiers for abnormally stable water-in-oil emulsions based on commercially available reagents, as well as methods for the advanced treatment of formation waters from oil fields in Kazakhstan.

To achieve the stated objective, the following tasks were defined:

1. To perform a systematic analysis of the physicochemical factors governing the aggregative stability of water-in-oil emulsions from selected oil fields in Kazakhstan, including the study of the group composition of crude oils, the ionic composition of formation waters, and the structure of interfacial films;

2. To substantiate and develop formulations of composite demulsifiers based on nonionic surfactants that provide a synergistic effect in the breakdown of stable emulsions with different stabilization mechanisms, and to identify the interaction patterns of their components using spectroscopic methods;

3. To carry out a comparative evaluation of the efficiency of the developed KNTU-14 reagent and industrial demulsifiers over a wide range of temperatures and dosages in order to justify the feasibility of energy-efficient oil treatment regimes;

4. To develop and investigate a method for the advanced reagent-based treatment of formation waters using activated aluminum alloys, ensuring compliance with regulatory requirements for their reuse in reservoir pressure maintenance systems.

Objects of the study:

Natural water-in-oil emulsions and formation waters from the Botakhan, Kysymbay, Saltanat Balgimbayev, Uzen, and Karazhanbas oil fields, as well as water samples from settling ponds of Atyrau Oil Refinery LLP.

Research methods:

The study was carried out using advanced analytical instrumentation, ensuring high accuracy and reproducibility of measurements. Measurement uncertainty was controlled in accordance with applicable GOST standards and methodological guidelines.

The following methods were employed: Fourier-transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, UV–Vis spectrophotometric analysis, thermogravimetric analysis (TGA–DTA), inductively coupled plasma optical emission spectrometry (ICP–OES), as well as laboratory evaluation of demulsifier efficiency using the bottle test.

Scientific novelty of the study:

For the first time, the patterns governing the stability of water-in-oil emulsions from oil fields in Western Kazakhstan have been established. These patterns are determined by the elevated content of asphaltenes, resins, and paraffins in crude oil,

as well as the high salinity of formation waters, leading to the formation of strong interfacial films.

It has been established that the high demulsification efficiency of composite reagents of the KNTU series, based on Randem-2208 and Tween surfactants, is associated with their synergistic interaction mediated by non-covalent interactions between components. This results in a reduction of the critical micelle concentration, an increase in interfacial activity, and ensures effective demulsification of highly stable water-in-oil emulsions, including at reduced temperatures.

It has been shown that the use of the developed reagents enables not only deep dehydration of water-in-oil emulsions but also simultaneous desalting of both oil and aqueous phases to regulatory requirements, thereby reducing the corrosion activity of process systems.

For the first time, a method for the reagent-based advanced treatment of formation waters using activated aluminum alloys has been developed, ensuring the reduction of petroleum hydrocarbons and ions of calcium, sodium, magnesium, and iron to acceptable levels.

Theoretical significance of the study lies in the scientific substantiation of the mechanisms governing the breakdown of highly stable water-in-oil emulsions based on the synergistic interaction of components in a binary system of nonionic surfactants. The adsorption–displacement mechanism of action of the developed KNTU compositions at the oil–water interface has been established, influencing the morphology and structure of interfacial films during demulsification at 25 °C.

For the first time, the role of coupled processes—hydrogen-induced microflotation, coagulation, and sorption—has been theoretically substantiated for the advanced treatment and partial softening of highly mineralized formation waters using activated aluminum alloys.

Practical significance of the study is associated with the development of an effective formulation of the KNTU-14 reagent, enabling oil treatment to meet Group I quality specifications at reduced dosages without the need for thermal heating. The proposed method for reagent-based water treatment using activated aluminum alloys ensures the reduction of residual oil content to below 15 mg/L, allowing reuse of treated water in reservoir pressure maintenance systems.

The results of the study are confirmed by patents of the Republic of Kazakhstan.

Key provisions submitted for defense:

1. The patterns governing the stability of water-in-oil emulsions have been established. This stability is determined by the synergistic effect of asphaltene–resin stabilization, ultra-high salinity (up to 320 g/L), and near-neutral pH of formation waters, resulting in the formation of highly resistant interfacial films and inhibition of coalescence processes.

2. The composition and technological efficiency of a series of KNTU composite demulsifiers based on Randem-2208 and Tween-85, Tween-80, and

Tween-20 have been developed and scientifically substantiated. It has been shown that the enhanced demulsification performance is due to a synergistic effect associated with non-covalent interactions between components, leading to the formation of mixed micellar structures and co-adsorption at the oil–water interface. This ensures effective disruption of interfacial films, deep dehydration of crude oil within the temperature range of 25–60 °C, and a reduction in reagent consumption to 80 ppm, which is 2–4 times lower compared to industrial analogues (Randem-2208, Dissolvan).

3. A reagent-based method for the treatment of formation waters using activated aluminum alloys has been developed, based on the synergy of coagulation and sorption processes. The method ensures the reduction of petroleum hydrocarbons to trace levels and a simultaneous decrease in the concentrations of Ca^{2+}, Mg^{2+}, Fe, and Mn ions, enabling reuse of the treated water for technological purposes.

Relationship of the dissertation with research and state-funded programs

The dissertation research was carried out within the framework of scientific projects aimed at developing technologies to improve the efficiency of oil treatment and to address environmental challenges in the oil and gas industry.

Certain stages of the work were conducted under the following research projects and contractual agreements:

-"Scientific and technical substantiation of innovations in the chemical cluster for the development of new materials and technologies to enhance the efficiency and environmental sustainability of industrial production", Project No. 2018/BR053630, Contract No. 259 dated March 28, 2018;

-"Hydrogen energy of activated metal alloys in addressing complex environmental problems", Project No. 2018/AP0513541, Contract No. 110 dated March 5, 2018;

-"Services for assessing the applicability of methods for removing asphaltene–resin–paraffin deposits (ARPD) from oil in settling ponds of Atyrau Oil Refinery LLP", Contract No. 943-17 dated August 2017;

-"Development of a method for the chemical removal of bottom sediments in fuel oil storage tanks of Pavlodar Petrochemical Plant LLP", Contract No. 15146.06 dated March 30, 2017;

-"Experimental laboratory studies and pilot-scale testing of a thermochemical treatment method using activated alloys at oil production facilities of Embamunaigas JSC", Contract No. 888-105 dated July 20, 2015;

-"Development of chemical systems for the oil production and transportation industry", Project No. 753 MES RK GF 13.15, Contract No. 544 dated April 7, 2015;

-"Investigation of a new method for oil dehydration and desalting at the oil treatment unit of Embamunaigas JSC", Contract No. 525-105 dated April 17, 2014.

Author's contribution, publications, and dissemination of results

The author's contribution consists in the analysis and critical evaluation of literature data, conducting experimental studies, applying physicochemical methods of analysis, systematizing and interpreting the obtained results, and formulating scientific conclusions based on the performed research.

Dissemination of results. The results of the dissertation were presented and discussed at the 8th International Scientific and Practical Conference "Innovative Technologies in Oil and Gas Gathering, Treatment and Transportation. Design, Construction, Operation and Automation of Production Facilities" (2019, Krasnodar), as well as at the international scientific and practical conferences Satbayev Readings: "Innovative Technologies as a Key to Solving Fundamental and Applied Problems in the Mining and Oil and Gas Sectors of the Economy of the Republic of Kazakhstan" (2019, Almaty), "Innovative Solutions to Traditional Problems: Engineering and Technology" (2018, Almaty), and "The Role and Place of Young Scientists in the Implementation of the New Economic Policy of Kazakhstan" (2015, Almaty).

Publications. The main results of the dissertation are published in 12 works, including 3 articles in international peer-reviewed journals indexed in Scopus (with percentiles of 56 and 31), 1 publication in a journal recommended by Committee for Quality Assurance in Science and Higher Education of the Ministry of Science and Higher Education of the Republic of Kazakhstan, 4 papers in the proceedings of international and national scientific conferences, 2 publications in other scientific journals and editions, and 2 patents.

Structure and scope of the dissertation. The dissertation includes normative references, a list of symbols and abbreviations, an introduction, three chapters, a conclusion, and a list of references. The total length of the dissertation is 113 pages, including 37 tables and 20 figures. The reference list comprises 114 sources.