ABSTRACT

of the dissertation for the degree of Doctor of Philosophy (PhD) in the educational program 8D07107 – «Chemical Engineering of Hydrocarbon»

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DEEP EUTECTIC SOLVENTS AS A NEW INHIBITORS OF ASPHALTENE DEPOSITION

Relevance of the Research Topic: In the 21st century, the growing demand for energy resources has led to the intensive development of the oil and gas industry. However, the technogenic and chemical problems that arise during oil production and transportation have a negative impact on the efficiency of this sector. One of the most challenging issues is asphaltene precipitation.

Asphaltenes are complex organic compounds with high molecular weight, rich in heteroatoms and aromatic structures, and composed of polar molecules. In petroleum systems, they exist in an unstable colloidal state and, under the influence of physicochemical parameters (such as a decrease in temperature, changes in pressure, evaporation of light fractions, or changes in solvent nature), precipitate and separate from crude oil.

Asphaltene deposition leads to the clogging of pipelines and wells, corrosion of technological equipment, and disruption of heat and mass transfer processes. This, in turn, reduces oil production efficiency, causes frequent equipment shutdowns, and increases additional economic costs. Therefore, the search for effective inhibitors capable of enhancing asphaltene stability or slowing down their precipitation is one of the pressing scientific and industrial challenges of modern times.

In recent years, deep eutectic solvents (DESs) have attracted particular interest in this field. DESs are liquid systems consisting of two or more components (a hydrogen bond donor and acceptor), which form hydrogen bonds, resulting in low melting points, high viscosity, thermal stability, and environmental safety. They comply with the principles of “green chemistry” and are used as non-toxic, biodegradable solvents in various fields, including pharmaceuticals, metallurgy, electrochemistry, and extraction technologies.

This dissertation investigates systems based on choline chloride:glycerol, choline chloride:ethylene glycol, betaine:glycerol, and betaine:ethylene glycol. Their inhibitory properties against asphaltenes are compared with those of a traditional asphaltene precipitation inhibitor—dodecylbenzenesulfonic acid.

This study is aimed at the development of “green” technologies and environmentally friendly chemical processes and can make a significant scientific contribution to oil production and transportation. Thus, the relevance of this dissertation lies in the need to search for and study environmentally safe and effective alternative solvent systems capable of addressing the problem of asphaltene

deposition during oil production. The results obtained may serve as the basis for the creation of a new generation of inhibitors suitable for industrial applications.

Research Objective: To synthesize deep eutectic solvents (DESs) as a new generation of environmentally friendly inhibitors of asphaltene precipitation extracted from heavy oil of the Karazhanbas field, and to investigate their physicochemical and inhibitory properties with the aim of improving oil quality, reducing environmental impact, and minimizing economic losses.

Research Tasks:

1. To synthesize samples of deep eutectic solvents (DESs) based on choline chloride and betaine in different molar ratios (1:2, 1:3) and determine their pH, density, viscosity, and thermal properties.
2. To study the structure of the synthesized DESs using NMR (^{1}H and ^{13}C) and FTIR spectroscopy.
3. To extract asphaltenes from the crude oil of the Karazhanbas field and investigate their structural and thermal properties.
4. To prepare a model oil system based on asphaltenes and evaluate its stability.
5. To investigate the inhibitory effect of DESs against asphaltene precipitation using UV spectrophotometry and optical microscopy, and to compare their efficiency with a traditional inhibitor.

Research Objects: Deep eutectic solvents, Karazhanbas field crude oil, asphaltenes, model oil.

Research Methods: The experimental studies were carried out using modern high-precision instruments (accuracy class 0.3–1.0). The methods employed included FTIR spectroscopy, ^{1}H and ^{13}C NMR spectroscopy, UV spectroscopy, and optical microscopy.

Scientific Novelty:

-For the first time, deep eutectic solvents (DESs) based on choline chloride and betaine were synthesized, and their physicochemical properties were determined.

-For the first time, DESs were applied as inhibitors of asphaltene precipitation in crude oil from the Karazhanbas field.

-The effectiveness of DESs as inhibitors in preventing asphaltene precipitation in a model oil system was demonstrated using physicochemical methods and compared with the performance of a traditional inhibitor.

Theoretical and Practical Significance: The theoretical significance of this work lies in the development of new deep eutectic solvents (DESs), as well as in the in-depth explanation of their physicochemical properties, structural features, and mechanisms of interaction with asphaltene molecules. Studying the relationship between the structure and properties of DESs makes it possible to identify key factors influencing the processes of asphaltene aggregation and precipitation.

The practical significance lies in assessing the efficiency of DESs in inhibiting asphaltene precipitation processes, which makes it possible to propose new, effective, and environmentally friendly methods for combating asphaltene deposits during oil production and transportation.

Overall, this work lays the foundation for a new direction that offers alternative, cost-effective, and eco-friendly solutions applicable in the petrochemical industry.

Key Points for Defense:

1 Four new deep eutectic solvents (DESs) were synthesized, and it was proven that they represent homogeneous, highly viscous, and thermally stable liquids. Their physicochemical properties (pH, viscosity, density, thermal stability) were determined, and their effectiveness against heavy oil components was investigated.

2 The structure and purity of the synthesized DESs were confirmed by ^{1}H and ^{13}C NMR as well as FTIR spectroscopy. The formation of hydrogen bonds was established and demonstrated to be a key factor preventing asphaltene precipitation.

3 The structural, elemental, and thermal characteristics of asphaltenes extracted from the Karazhanbas field crude oil were studied. It was determined that asphaltenes exhibit thermal stability within the range of 30–450 °C, and that the C/H ratio, close to 1, indicates a high level of aromatic structures, which are the main cause of their chemical stability.

4 For the first time, DESs were applied to inhibit asphaltene precipitation in Kazakhstani crude oil, and their efficiency was comparatively evaluated against traditional inhibitors. According to UV–Vis spectroscopy and optical microscopy data, choline chloride–based DESs demonstrated 1.5 times higher inhibitory properties than betaine-based DESs.

Author's Personal Contribution, Publications, and Validation of Practical Results: The author’s personal contribution lies in the analysis and critical evaluation of literature data, the performance of experimental studies, the application of physicochemical analytical methods, the systematization and interpretation of the obtained results, as well as the formulation of scientific conclusions based on the conducted research.

Validation of the Work: The materials of the dissertation were presented and discussed at the "Frontier Symposium of Engineered Science," held in a hybrid (in-person and remote) format from June 23 to 29, 2024, in Astana, Kazakhstan.

Publications: The main results of the dissertation have been published in 5 co-authored works, including 1 article in an international scientific journal indexed in the Scopus database; 3 articles in journals recommended by the Committee for Control in the Field of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan; and 1 paper presented at international and national scientific conferences.

Structure and Volume 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 volume of the work is 98 pages and contains 12 tables and 46 figures. The list of references comprises 174 titles.