ABSTRACT

to the thesis on **"NEW SURFACTANTS BASED ON MODIFIED POLYETHYLENTEREPHATALATE WASTE FOR OILFIELD CHEMISTRY"**, submitted for the degree of Doctor of Philosophy (PhD) in the specialty 6D073900 - "Petrochemistry"

Merekenova Assem Kairatbekovna

The purpose and objectives of the dissertation. The aim of the work is to develop scientific foundations for the creation and synthesis of new reagents of chemical action by the interaction of N-N'-bis(2-hydroxy)ethylterephthalate (BHET) with polyoxyethylenesorbitanmonooleate, phosphorylation agents, as well as N-N'-bis(2-hydroxy)ethylterephthalamide (BHETA) with polyphosphoric acid. Finding ways of practical application of polyfunctional reagents.

In connection with the goals set, the following tasks were identified:

- synthesis of a new surfactants based on PET (polyethylene terephthalate) monomers obtained by chemical recycling of polyethylene terephthalate waste;
- study of the physicochemical properties of the developed surfactants;
- establishment of the structure and mechanisms for obtaining a new surfactants;
- practical use of a new reagents as a water-oil emulsion demulsifier, corrosion and scale inhibitor.

Research methods. A modern equipment was used with an accuracy class of 0.25-0.5 and analysis methods carried out in accordance with government standards, as well as threefold reproducibility of research results.

Study of glycolysis and aminolysis products, synthesized surfactants were carried out by modern physicochemical methods: IR spectroscopy, TG / DSC, 1H, 13C, 31P NMR spectroscopy.

The surface tension of aqueous solutions of nonionic surfactants was measured by the ring-peel method (Du Noüy ring) on a Kruss tensiometer.

The study of corrosion protection was studied using the "Autolab PGSTAT 302 N" potentiostat.

The study of the morphology of the formed crystals of the samples of solid precipitates of CaCO3 and CaSO4 salts was studied using the method of scanning electron microscopy JEOL JSM-649OLV.

The main provisions (proven scientific hypotheses and other conclusions that are new knowledge) submitted for defense:

- surfactants obtained by condensation of BHET with polyoxyethylene sorbitan monooleate, the structure of the products established by IR spectroscopy with a Fourier transform, as well as ^{1}H-, ^{13}C-NMR spectroscopy, COSY ^{1}H-^{1}H-NMR spectroscopy;
- new surfactants obtained by phosphorylation of BHET and BHETA with phosphorylation agents, the structure of products established by IR, ^{1}H-, ^{31}P-, ^{13}C-, COSY ^{1}H-^{1}HNMR spectroscopy;

- test results of polyoxyethylene sorbitan monooleate of BHET ester as a demulsifier of abnormally stable oil-water emulsions;
- results of tests on the use of esters of phosphoric acids as corrosion and scale inhibitors.

Description of the main results of the study.

For the first time, research has been carried out to find ways and possibilities for the integrated use and application of polyethylene terephthalate waste. It is concluded that it is economically feasible to chemical modification of this polymer.

The process of depolymerization of PET with ethylene glycol and monoethanolamine, with the formation of BHET and BHETA, has been modified and experimentally carried out. The structure and composition of BHET, BHETA have been proved by IR-, ^{1}H-, ^{13}C-NMR spectroscopy.

For the first time, the synthesis of a new surfactant was theoretically substantiated and experimentally carried out, which is based on the esterification reaction of BHET with polyoxyethylene sorbitan monooleate. The composition and structure of the new reagent were studied by spectrometric methods: IR, ^{1}H-, ^{13}C NMR. The mechanism of the process based on the kinetic parameters of the esterification reaction has been proposed and substantiated. The demulsifying activity of the surfactant was studied during the destruction of the oil-water emulsion of the Uzen 5857 field, it was shown that the developed demulsifier is not inferior to the best industrial analogue in terms of the degree of destruction of the oil-water emulsion. In order to reduce the settling time and increase the degree of demulsification, composite compositions have been developed for the destruction of oil emulsion samples based on the synthesized surfactant and industrial demulsifier Randem 2208. It is shown that the composite composition together with Randem 2208 allows to reduce the settling time to 20 minutes, to reduce the amount of injected demulsifier up to 100 ppm and to increase the degree of demulsification to 90%.

For the first time, the synthesis of new organophosphorus compounds - phosphoric acid esters based on the phosphorylation reactions of BHET and BHETA with polyphosphoric acid, orthophosphoric acid and phosphoric anhydride was theoretically substantiated and experimentally carried out. The mechanism of the process is proposed and substantiated. The structure and composition of organophosphorus reagents have been proven using modern physicochemical methods of analysis: IR-, ^{1}H-, ^{31}P, ^{13}C-spectroscopy, COSY (1H-1H) two-dimensional homonuclear correlation spectroscopy.

The effect of phosphoric acid esters BHET on the corrosion-mechanical destruction of samples of plates of grade st. 3 in different temperature ranges, as well as the destruction of an electrode of grade st. 3 under the action of a conducting electric current has been studied. It is shown that the maximum protective effect with the method of gravimetric tests is 85%, with an inhibitor concentration of 200 ppm, and the effectiveness of the protective action with the method of electrochemical tests is 70.9%, with an inhibitor concentration of 200 ppm.

The inhibitory activity of the developed phosphoric acid esters BHET and phosphoric acid esters BHETA was studied on model water-salt solutions. It was found that inhibitors have complex actions in relation to carbonate and sulfate deposits. By the method of scanning electron spectroscopy, the morphology of crystals was studied before and after treatment of inhibitors, it was shown that inhibitors have complexion properties and are able to be incorporated into the surface of crystallization nuclei, as a result of which the growth of crystals stops.

Substantiation of the novelty and importance of the results obtained.

About 2 billion tons of municipal solid waste are generated annually all over the world, of which 12% are polymer waste, it is predicted that by 2050 the amount of solid waste will be increased to 3 billion tons. At the same time, in Kazakhstan, according to data published by the Committee on Statistics of the Ministry of National Economy of the Republic of Kazakhstan for 2018, about 4.319 million tons of solid waste was formed. It is predicted that the amount of solid waste will be increased to 8 million tons by 2025.

Disposal of waste in landfills is still the main method of allocation of solid waste.

Polyethylene terephthalate occupies the main share among of polymeric waste - 30%, high density polyethylene and low density polyethylene - 17%, polypropylene - 15%, polystyrene - 9%, polyvinyl chloride - 6% and other carbo- and heterochain polymers - 23 %.

Recycling of polymeric waste is the most resource-saving way, which allows improving the environment, obtaining various products, including starting monomers, which save primary raw materials, since recycled polymers are much cheaper than raw materials by 40-90%, depending on the type of polymer.

According to statistical studies of US Environmental Protection Agency, the degree of processing of plastics in the world are distributed as follows: polyethylene terephthalate - 19.5%, high-density polyethylene - 10%, low-density polyethylene - 5%, polypropylene -1%, polystyrene -1%, and PVC waste is not recycled. PET, unlike other polymeric materials, is quite easily amenable to methods of chemical processing, injection molding, extrusion, blow molding, thermoforming, and therefore PET waste is the most recyclable in the world.

PET waste is not only a source of valuable raw materials for production, but also poses a serious environmental threat to the environment. Polymer wastes taken to landfills do not corrode and degrade in natural conditions, serve as a source of air pollution, and the products of incomplete decomposition of plastic materials, getting into groundwater, have a direct effect on the soil cover, which leads to the unsuitability of using large areas. Thus, the issue of safe and highly efficient processing of PET waste requires an urgent solution.

In connection with the above, the development of scientific foundations for the creation and synthesis of new reagents of chemical action based on the products of depolymerization of household waste polyethylene terephthalate will become an important key in solving these issues.

The novelty of the dissertation research is the developed methods for the synthesis of a new reagent of complex action with adjustable properties by condensation of BHET with polyoxyethylene sorbitan monooleate, methods of esterification of BHET and BHETA with phosphorylation agents, and as an assessment of the developed reagents for de-emulation of corrosive agents, as well as evaluation of the developed reagents.

Contribution of the doctoral student to the preparation of each publication.

The author's personal contribution consists in the search, analysis of literary and patent sources, direct execution of the experimental part of the work, analysis, generalization and interpretation of the experimental data obtained.

On the topic of the dissertation work, 15 papers have been published including 2 articles in international rating publications included in the databases "Scopus" and "Web of science", 1 article in publications from the list approved by the Committee for Control in the Field of Education and Science of the Republic of Kazakhstan, 5 patents of the Republic of Kazakhstan, equated to articles approved by the Committee for Control in the Field of Education and Science of the Republic of Kazakhstan, 5 abstracts at international conferences, including, as well as 2 abstracts in foreign countries.

The results were presented and discussed at international scientific and practical conferences:

- Труды Международных Сатпаевских чтений "Роль и место молодых ученых и реализации новой экономической политики Казахстана". – Алматы: КазНТУ, 2015 г.;
- Труды Международные Сатпаевские чтения "Конкурентоспособность технической науки и образования", посвященной 25-летию независимости Республики Казахстан. – Алматы: КазНТУ, 2016 г.;
- Труды международной конференции студентов и молодых ученых "Әл Фараби Әлемі". – Алматы : КазНУ, 2016 г.;
- 7th International Confrence. “Biomaterials and nanoboimaterials: Recent advances safety-toxicology and ecology issues. – Heraklion,Crete, 2017;
- VII International workshop “Specialty polymers for environment protection, oil industry, bio-nanotechnology and medicine”. – Almaty, 2017;
- 8th International Confrence. “Biomaterials and nanoboimaterials: Recent advances safety-toxicology and ecology issues. – Heraklion, Crete, 2018;
- I Коршаковская Всероссийская с международным участием конференция «Поликонденсационные процессы и полимеры». – Москва, 2019 г..