THE INFLUENCE OF THE PHYSICOCHEMICAL NATURE OF SURFACTANTS ON THE EFFECTIVENESS OF THEIR ACTION IN VARIOUS ENVIRONMENTS.

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Abstract: The results of the use of surface-active substances (surfactants) in the process of oxidative demercaptanization of hydrocarbon raw materials are presented. It is shown that the use of surfactants increases the efficiency of the demercaptanization process and makes it possible to extract from processed hydrocarbons not only the simplest, but also higher molecular weight mercaptans, as well as organosulfur compounds of other classes.

Keywords: Surfactants (surfactants), synthetic detergents (SMS), micelles, ionic surfactants, nonionic surfactants, hydrophilicity, hydrophobicity, detergency, biodegradability. One of the large-capacity areas of the petrochemical industry is the production of surface-active substances (surfactants).

Аннотация: Представлены результаты применения поверхностно-активных веществ (ПАВ) в процессе окислительной демеркаптанизации углеводородного сырья. Показано, что использование поверхностно-активных веществ повышает эффективность процесса демеркаптанизации и позволяет извлекать из перерабатываемых углеводородов не только простейшие, но и высокомолекулярные меркаптаны, а также сероорганические соединения других классов.

Ключевые слова: поверхностно-активные вещества (ПАВ), синтетические детергенты (СМС), мицеллы, ионные поверхностно-активные вещества, неионные поверхностно-активные вещества, гидрофильность, гидрофобность, моющая способность, способность к биологическому разложению. Одним из крупнотоннажных направлений нефтехимической промышленности является производство поверхностно-активных веществ (ПАВ).

Annotatsiya: Uglevodorod xom ashyosini oksidlovchi demerkaptanizatsiya jarayonida sirt faol moddalar (sirt faol moddalar) dan foydalanish natijalari keltirilgan. Sirt faol moddalardan foydalanish demerkaptanizatsiya jarayonining samaradorligini oshirishi va qayta ishlangan uglevodorodlardan nafaqat eng oddiy, balki yuqori molekulyar merkaptanlarni, shuningdek, boshqa sinflarning organosulfur birikmalarini ham ajratib olish imkonini berishi ko'rsatilgan.

Kalit so'zlar: sirt faol moddalar (sirt faol moddalar), sintetik yuvish vositalari (SMS), misellar, ionli sirt faol moddalar, ion bo'lmagan sirt faol moddalar, hidrofilik, hidrofobiklik, yuvish qobiliyati, biologik parchalanish qobiliyati. Neft-

kimyo sanoatining yirik tonnaj yo'nalishlaridan biri sirt faol moddalar (sirt faol moddalar) ishlab chiqarishdir.

Введение

World production of surfactants is 2-3 kg per capita per year. Approximately 37% of the produced surfactants are used for household chemicals, the rest in industry and agriculture. Simultaneously with the annual increase in the production of surfactants, the ratio between their use in everyday life and industry is changing in favor of industry. Surfactants are used in more than 100 sectors of the national economy. Most of the produced surfactants are used in the composition of detergents, in the production of fabrics and products based on synthetic and natural fibers. Large consumers of surfactants include the oil, chemical industry, building materials industry and a number of others. Surfactants (surfactants) are chemical compounds that are concentrated (adsorbed) on the interface, cause a decrease in its free surface energy GS and, accordingly, surface tension. The main quantitative characteristic of surfactants is surface activity - the ability of a substance to reduce surface tension at the phase boundary 1.2. Along with the ability to be adsorbed on the interfacial surface, many surfactants have another important property: under certain conditions, self-organized nanoaggregates (micelles) consisting of tens and hundreds of surfactant molecules or ions are formed in surfactant solutions. Thanks to these. radicals that make up the oleo-, or lipophilic part (it is also the hydrophobic part of the molecule), and one or more polar groups - the hydrophilic part. Hydrophobic groups that interact weakly with water determine the tendency of the molecule to transition from an aqueous (polar) medium to a hydrocarbon (non-polar). Hydrophilic groups, on the contrary, keep the molecule in a polar environment or, if the surfactant molecule is found in a hydrocarbon liquid, determine its tendency to transition to a polar medium; the surface activity of surfactants dissolved in non-polar liquids is due to hydrophilic groups, and dissolved in water - hydrophobic radicals.

Surfactants are divided into two types according to the nature of adsorption and the mechanism of stabilization of disperse systems: low-molecular compounds of amphiphilic nature, having a hydrophilic group (“head”) and a hydrophobic “tail”; high-molecular compounds in which hydrophilic and hydrophobic groups alternate, evenly distributed along the entire length of the polymer chain. The dominant position among the surfactants produced in the world is occupied by the cheapest and fairly versatile anionic surfactants, which account for at least 60% of world production; up to 30% are non-ionic surfactants, about 10% are cationic, and only a fraction of a percent are synthetic ampholytic surfactants. According to the type of hydrophilic groups, surfactants are divided into ionic, or ionic and or non-ionic. Ionic surfactants dissociate in water into ions, some of which have adsorption

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(surface) activity, while others (counterions) are adsorption inactive. If anions are adsorption active, surfactants are called anionic, or anionic, in the opposite case, cationic, or cationic active. Anionic surfactants - organic acids and their salts, cationic bases, usually amines of various degrees of substitution, and their salts. Some surfactants contain both acidic and basic groups.

Depending on the conditions, they exhibit the properties of either anionic or cationic surfactants, which is why they are called amphoteric or ampholytic surfactants. Anionic surfactants. The following compounds belong to this type of surfactant. Carboxylic compounds (RCOOH) and their salts (soaps) (RCOOM, where R is a hydrocarbon aliphatic radical with 12-18 carbon atoms, M is Na +, K + or NH_4 +. Soaps of carboxylic acids have a good washing effect only in an alkaline environment, environment (due to insoluble fatty acids and in hard water (due to the formation of insoluble calcium and magnesium salts), the washing ability of these surfactants is low. Soaps are characterized by complete biodegradability. Alkylar sulfonates are salts of aromatic sulfonic acids $RArSO_3M$. They are the cheapest and most readily available synthetic surfactants. Show the good washing action in alkaline and sour environments and in hard water. Alkyl sulfonates RSO_3M (R usually C_{10} - C_{20}). These surfactants have good detergent action in various pH conditions, in hard water and good biodegradability. Alkyl sulfates $ROSO_3M$ (R обычно C_{10} – C_{18}). Alkyl sulfates belong to third generation surfactants - compounds biochemically decomposing to inorganic fragments (water, carbon dioxide and sodium sulfate). Primary alkyl sulfates $ROSO_2Na$ are obtained by sulfation of primary higher fatty alcohols and subsequent neutralization of the resulting sulfonic ether sulfate with cymnatro. The alcohols necessary for this purpose are currently obtained mainly by synthetic methods - the reduction of esters of higher fatty acids, oxosynthesis, and the production of ethylene through organic aluminum compounds (alfol process). Secondary alkyl sulfates $(CH_3)_2ONa$ are obtained by reacting sulfuric acid with α-olefins or by sulfating secondary higher alcohols. Among alkyl sulfates, only those obtained from primary alcohols with a straight chain of carbon atoms have the maximum detergency. The washing ability of alkyl sulfates decreases with the displacement of the sulfate group deep into the molecule and with the branching of the carbon chain. Therefore, the most suitable raw materials for the production of alkyl sulfates are primary alcohols and C_{12}-C_8 α-olefins with a straight carbon chain. The mass use of alkyl sulfates in synthetic detergents is hindered by their somewhat higher cost compared to alkylbenzene sulfonates. However, as feedstock production processes (primary and secondary alcohols and α-olefins) improve, this obstacle will be removed. Cationic surfactants include aliphatic and aromatic amines (primary, secondary and tertiary) and their salts, quaternary ammonium

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bases and their salts, quaternary phosphonium and tertiary sulfonium bases, pyridine compounds. Cationic surfactants are well adsorbed on negatively charged surfaces (metals, many minerals, plastics, cell membranes, cement). Therefore, they are used as antistatic agents, corrosion inhibitors, bactericidal, fungicidal, disinfectants. Quaternary ammonium compounds with a length of hydrocarbon radical C_{12}-C_{18} have a bactericidal effect, and they are approximately 300 times more effective than phenol in terms of destructive action against microorganisms. Salts of pyridine bases are used in the textile industry as fixatives for dyeing, as well as for finishing finished fabrics. Amphoteric, or ampholytic surfactants - substances in the composition of the molecules of which there are both acidic and basic groups. They can be obtained from anionic compounds by introducing amino groups into them or from cationic by introducing acid. At pH<4, ampholytic surfactants exhibit the properties of cationic compounds, at pH 9-12 - anionic, and at pH 4-9 ionic compounds. This type of surfactant includes many natural substances, such as amino acids and proteins. Their synthetic analogs are alkyl amino acids, for example, cetyl aminoacetic acid $C_{16}H_{33}NH–CH_2COO$. The production of such substances is quite difficult and expensive, and they are not yet widely used assurfactants.

Nonionic surfactants are the most promising and rapidly developing class of surfactants. At least 80-90% of these surfactants are obtained by adding ethylene oxide to alcohols, alkylphenols, carboxylic acids, amines, etc. Polyoxyethylene esters of alkylphenols are the most numerous and widespread group of nonionic surfactants. For example, RC_6H_4O (CH_2CH_2O) nH, where n is the average number of hydroxyethyl groups.

The polyoxyethylene esters of alcohols RO (CH_2CH_2O) pH have acquired an important industrial significance, because they are easily biodegradable under natural conditions. As detergent components, nonionic surfactants are not inferior to high-quality soaps, and are used in water of any hardness, with different pH values. They generally have a low foaming capacity and can be used as defoamers.

According to the physicochemical mechanism of action in a dissolving medium, all surfactants are divided into two categories (according to the classification of P.A. Rebinder). One category includes micelle-forming surfactants (colloidal soluble surfactants), while the other does not form micelles (truly soluble). In solutions of micelle-forming surfactants above the critical micelle concentration (SMS), colloidal particles (micelles) appear, consisting of tens or hundreds of molecules (ions). Micelles reversibly decompose into individual molecules or ions when a solution (more precisely, a colloidal dispersion) is diluted to a concentration below the SMS. Thus, solutions of micelle-forming surfactants occupy an intermediate position between true (molecular) and

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colloidal solutions (sols); therefore, they are often called semicolloidal systems. Micellar surfactants include all detergents, emulsifiers, wetting agents, dispersants, etc. Truly soluble surfactants do not exhibit stabilizing properties and are weak wetting agents and weak foaming agents. Surfactants are widely used in industry, agriculture, medicine, and everyday life. The most important areas of surfactant consumption are: production of soaps and detergents for technical and sanitary needs; textile auxiliaries used for processing fabrics and preparing raw materials for them; paint products. Surfactants are used in many technological processes in the chemical, petrochemical, chemical-pharmaceutical, and food industries. Currently, 80% of the surfactants produced in the world are used in the synthetic detergents (SMS) industry. SMS are of great importance in meeting the needs of people, and are also used in various industries. With the development of production and the culture of everyday life, the demand for synthetic detergents and their output are growing rapidly. Currently, about 1.7 million tons of products are produced annually, 0.2 million tons are exported, and 0.1 million tons are imported. The development of the market for synthetic detergents occurs along with the tightening of requirements for their environmental performance. SMS are mixtures of surfactants with auxiliary components and fillers (soda, phosphates, sodium sulfate), which enhance the washing effect of the main components. Surfactants are used both for stabilizing and destroying dispersed systems of emulsions, suspensions, foams, for reducing the strength of treated surfaces, for fighting corrosion, protecting the environment, etc.

Among the surfactants currently produced by the industry and used as synthetic detergents, anionic active substances are the most widely used, the production of which reaches 68% of the production of all synthetic detergents. In terms of production scale, among anionic synthetic detergents, alkylaryl sulfonates are in first place. SMS obtained on the basis of alkylaryl sulfonates are poorly biochemically oxidized in water bodies, accumulate and, as a result, oxygen exchange is disturbed, foam appears. Third generation surfactants (compounds that are completely biochemically decomposed to inorganic compounds (water, carbon dioxide and sodium sulfate) include alkyl sulfates of primary (primary (CH2OSO2ONa) and secondary (secondary (CHOSO2ONa)) alcohols, which are salts of sulfoesters, in terms of production they rank second among anionic surfactant.

In terms of detergent properties, primary alkyl sulfates are among the best surfactants, they are inferior in quality to secondary alkyl sulfates. Detergents based on alkyl sulfates are produced in the form of liquid formulations (with 20-40% active substance) or powders. They are used for washing clothes and fabrics,

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washing wool, various products, etc. Today, various authors cite the use of surfactants in a wide variety of industries and agriculture.

Currently, surfactants are used to intensify various technological processes in the oil industry. A feature of the modern development of the oil industry is a significant change in the structure of reserves towards an increase in the proportion of hard-to-recover oils. Surfactants are used in well drilling for a more complete extraction of oil from reservoirs (increased oil recovery), accelerating the development of oil fields, in oil preparation, to combat corrosion of oil equipment, deposits of paraffins and salts, environmental pollution, to reduce hydraulic losses during oil transportation etc. The widespread use of ethoxylated surfactants is associated with an increase in oil production: they are introduced into solutions injected into wells during the so-called edge flooding, which contributes to the displacement of oil from the reservoir to the production well. Some processes, such as demulsification and desalination, cannot be carried out at all without the use of surfactants. A very promising direction of intensifying the process of obtaining oxidized bitumen and improving their quality is the introduction of surfactants into the system, which are modifying additives that change the reactivity of the feedstock, as well as the physicochemical properties. The amount of surfactants, as a rule, does not exceed tenths of a percent. Their use is not associated with significant material costs and is quite simple in hardware design, but the oxidation of raw materials activated with surfactant additives proceeds more efficiently. Therefore, the use of surfactants in the processing of oil residues is a promising direction in technology, which makes it possible to intensify various technological processes and improve the quality of commercial petroleum products, in particular, petroleum bitumen. Modifying surfactant additives make it possible to improve the performance properties of bitumen, as well as the conditions for wetting the surface of mineral materials with bitumen, forming an absorption layer facing the polar groups to the surface of the mineral material and the hydrocarbon part into the volume of bitumen. This reduces the temperature and time for obtaining a homogeneous mixture, and also significantl.

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