Наведено результати досліджень процесу сульфатування сумішей органічних речовин низькоконцентрованим газоподібним триоксидом сірки в об'ємному реакторі. Описано матеріали та методи дослідження процесу. Визначено залежності якості поверхнево-активних речовин від основних технологічних параметрів: мольного співвідношення реагентів, концентрації триоксиду сірки та температури процесу сульфатування. Наведено дані про зміну величин щільності та в'язкості реакційних мас в ході даного процесу

Ключові слова: сульфатуючий агент, сульфатування, реактор, реакційна маса, щільність, в'язкість, поверхнево-активна речовина

Приведены результаты исследований процесса сульфатирования смесей органических веществ низкоконцентрированным газообразным триоксидом серы в объемном реакторе. Определены зависимости качества поверхностно-активных веществ от основных технологических параметров: мольного соотношения реагентов, концентрации триоксида серы и температуры процесса сульфатирования. Приведены данные об изменении величин плотности и вязкости реакционных масс в ходе данного процесса

Ключевые слова: сульфатирующий агент, сульфатирование, реактор, реакционная масса, плотность, вязкость, поверхностно-активное вещество

REGULARITIES OF THE PROCESS OF SULFATION OF THE MIXTURES OF ORGANIC SUBSTANCES

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1. Introduction

Contemporary world trends in the field of scientific and technical progress are aimed at improving such characteristics of industrial production as quality of products, resource- and energy-efficiency. The application of surface active substances (SAS) contributes to the intensification of technological processes, increases productivity, improves product quality, saves raw materials and energy. A peculiarity of SAS to absorb on the surface of a phase interface allows using them as emulsifiers, dispersants, wetting agents, to improve the oil recovery of layers. Most of them are used as the base for detergents and foam forming formulations. SAS are divided into anionic, nonionic, cationic, amphoteric. The largest amount of all manufactured in the world (about 80 %) are anionic SAS. The current state of technology and equipment for obtaining anionic sulfur-containing SAS is characterized by diversity of technical solutions not only under laboratory conditions, but in industrial production as well. The existence of different variants of apparatus-technological design of this process is caused by several reasons. First: both under laboratory and industrial conditions, they sulfate by a variety of sulfatizing agents: sulfuric acid, oleum, sulfamic acid, chlorosulfonic acid, complexes of sulfur trioxide, gaseous sulfur trioxide. Second: there is little data on the mechanism, on the process macro kinetics. This is linked probably to considerable difficulties in analyzing reaction mixtures due to rapid course of the reaction.

Of considerable interest is the raw materials base for obtaining SAS. It should be noted that sulfation is applied both to separate products and to their mixtures. Sulfation of mixtures of organic raw materials is paid considerably less attention to than to raw materials, though the industry and households usually use mixtures of SAS. The use of mixtures of organic substances allows introducing into the process of sulfation other substances, which at separate sulfation do not enable obtaining high quality products.

Due to the synergy of two or several SAS, the finished product has considerably better properties than separate SAS. The use of such SAS allows creating new compositions that expand the range of their applications, in particular for high-quality foam forming formulations, the demand for which has grown considerably in recent years. In this connection, of interest is the study of the process of sulfation of mixtures of organic raw materials for obtaining products of high quality, which may be used in foam forming formulations.

2. Literature review and problem statement

Technical and economic indicators of the process of obtaining SAS are closely related to using a sulfatizing agent. A justified selection of a sulfatizing agent is possible when comparing technical indicators of the process and the product quality. In the course of sulfation of higher alcohols by

sulfuric acid, the esters of sulfuric acid are formed [1]. The basic reaction is as follows (1)

$$ROH+H_2SO_4 \leftrightarrow ROSO_3H+H_2O, \qquad (1)$$

where R is the carbohydrate radical.

However, as a result of reverse nature of the basic reaction, the degree of sulfation is not more than 80 % even at 2-fold molar excess of sulfuric acid. As a result, the neutralized paste contains a significant amount of sodium sulfate, which creates certain difficulties when using such SAS. In the course of sulfation of higher alcohols, due to their poor dissolution in sulfuric acid, diffusion inhibition of the process occurs that requires intensive stirring of reagents. Because of this, energy costs for the process of sulfation increase. To increase the degree of sulfation, they use sulfatizing agents whose application renders the reaction irreversible.

Sulfamic acid with higher alcohols forms the corresponding ammonium products (2)

$$ROH+NH_2SO_3H \rightarrow RHSO_3NH_2. \qquad (2)$$

Sulfation by sulfamic acid occurs under mild conditions [1]. Another advantage is linked to the fact that sulfamic acid selectively sulfates organic raw materials. This prevents the formation of the mixed sulfate-sulfonate compounds. However, it is less reaction capable and relatively expensive, which limits its use.

For sulfation of higher alcohols, chlorosulfonic acid is applied in industry (3).

$$ROH+HSO_3Cl \rightarrow ROSO_3H+HCl. \qquad (3)$$

When using it, only a small surplus of sulfatizing agent is needed and the derived products have high quality indicators [2]. However, aggressiveness of hydrogen chloride, the need for its disposal and partially the cost of chlorosulfonic acid restrains its application.

Gaseous sulfur trioxide is the mostly widely used as a sulfatizing agent (4)

$$ROH+SO_3 \rightarrow ROSO_3H. \qquad (4)$$

Sulfation by gaseous sulfur trioxide has a number of benefits [2]: high degree of sulfation of organic raw materials, a neutralized product contains almost no sodium sulfate, an insignificant excess of a sulfatizing agent, high quality of obtained products. High exothermicity of the process may contribute to a local increase in temperature, which may be removed through intensification of transfer processes [3].

From the analysis of sulfatizing agents one may conclude that sulfation of organic raw materials with gaseous sulfur trioxide with intensive interphase exchange is one of the most promising areas for use in industrial production.

Apparatus-sulfation process scheme with the use of gaseous sulfur trioxide as a sulfatizing agent (Fig. 1) consists of the following basic nodes: air dehumidification, drying of organic raw materials, burning sulfur to obtain gaseous sulfur dioxide, oxidation of sulfur dioxide to sulfur trioxide, sulfation, neutralization, purification of the flue gases.

Air drying is carried out usually in two stages: at the first stage, air is cooled by water and then by the monoethyleneglycol solution; at the second stage, drying is performed

by silica gel until achieving the moisture content in the air not exceeding 0.02 g/m³.

Drying of organic raw materials is carried out by the method of evaporation.

Burning of sulfur takes place at temperature of 1023 K. The ratio of air and sulfur is defined by the content of sulfur trioxide in gas-air flow, it is usually 3–6 % by volume.

Obtaining a sulfatizing agent is achieved by catalytic oxidation of sulfur dioxide to sulfur trioxide on the vanadium catalyst. At the stage of sulfation, the interaction of sulfur trioxide with organic substance with the formation of an intermediate product, which is fully responsible for the quality of finished products and resource-saving. At the stage of neutralization, as a result of interaction of sulfation products with alkali solution, a finished product is created. The gas-air flow after the stage of sulfation is supplied to the stage of purification from SO_2 and SO_3 and then it is dumped into the atmosphere. Thus, the main stage of SAS manufacturing, which is responsible for the quality of products and resource-efficiency, is that of sulfation of organic matter.
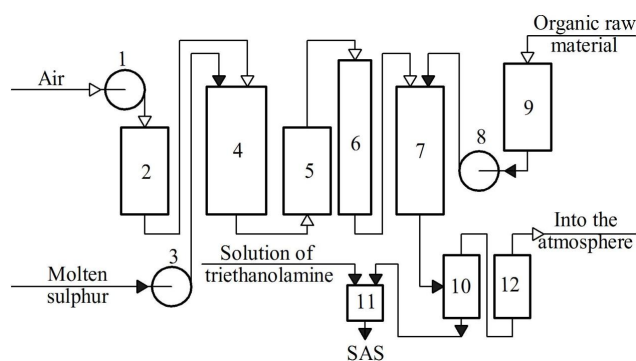

Fig. 1. Apparatus-technological diagram of the process of sulfation: 1 — air blast, 2 — drier, 3, 8 — pump dispensers, 4 — sulphur burning furnace, 5 — refrigerator, 6 — contact apparatus, 7 — sulfation reactor, 9 — evaporator, 10 — cyclone, 11 — neutralizer, 12 — absorption column

Given a high reaction speed and considerable heat release, the process of sulfation of organic raw materials implies the presence of two structural elements in the apparatus design: contact and heat exchanging. These elements may be combined or exist separately. Depending on the contact method of gaseous sulfur trioxide with organic raw material and removal of reaction heat, there are technological schemes that are divided into two groups: schemes of long period and schemes with brief period of organic materials' time in sulfating devices. When removing reaction heat from the mass of organic raw material that reacted (while separating elements), the technological scheme is characterized by long period of product's exposure in the zone of the process (from 20 min to 60 min.). When removing the heat directly from the element where the contact between sulfur trioxide and organic raw material occurs, the time of a product's exposure is a few minutes [4].

Devices with a long period of product's exposure are divided into:

– volumetric (bubbling), in which the contact of gaseous sulfur trioxide and organic raw material occurs on the sur-

face of bubbles in the volume of liquid phase, and removal of heat on the coil or through the wall of a cooling shirt;

– jet, in which the cooling of raw material that reacted occurs after separation in the remote heat exchanger.

It is necessary to install mixing devices in the volumetric devices. This increases the surface of exchange and intensifies the process of sulfation. Volumetric mixer devices are widely used in the study of the process of sulfation under laboratory conditions.

Sulfation in jet machines is characterized by creation of highly dispersed liquid phase with a developed surface of the contact. Interaction is accomplished by submitting the reagents under pressure to the contact zone of organic raw material and gas. However, in this case it is not possible to use SO_3 in full in one pass and there appears a need for circulation of the reaction mass, which increases its time in the machine.

The schemes with a brief period of organic raw materials' exposure found more widespread use in the technology of SAS. A number of procedures were developed, in which the heat release is achieved directly at the contact of gaseous sulfur trioxide with organic raw material: rotary film devices, film devices with upward flow or downward flow of reagents. In the rotary film devices, the supply of gaseous sulfur trioxide is carried out either at the bottom of the device or diffused by its height; in this case, with such an apparatus-technological design, it is possible to achieve the degree of sulfation of organic raw materials at the level of 96–98 %. However, rotary film devices are complicated in manufacturing, characterized by increased operating costs, there is a gradual build-up of coke on the rotor, which leads to frequent stops in violation of the rhythm of production in general.

Recently, film devices with an upward or downward flow of reagents have been widely used where only hydrodynamic forces of flows are applied. Film devices with an upward forward flow have a developed structure, and hence better heat- and mass exchanging characteristics compared to a downward phase motion. However, in the multi-pipe version there are large difficulties in organizing the uniform distribution of gas and organic materials along separate tubes. Actually, it is their main shortcoming.

Devices with downward flow of phases may be slotted and tubular. In the devices of slotted type they receive high quality products but they are inferior to the tubular ones due to simplicity of the designs of the latter. In this case, organic raw material flow down the inner wall of the tube and gaseous sulfur trioxide is fed by the center of the tube [5]. Authors [6] note the main variables that affect the process of sulfation in a tubular device with a downward flow of phases: molar ratio of the reagents, concentration of sulfur trioxide in the gas air stream, temperature of the fluid stream, length of the reaction tube. The analysis of the process of mass exchange in the micro reactor with the falling film is conducted [7]. Thus, it may be stated that such an apparatus-technological design is currently the most promising one for the use under industrial conditions.

Important while obtaining SAS is the choice of organic raw materials. This is caused by a number of factors: condition and trend of development of raw materials base, structure and quality of original raw materials, consumers' requests, the prospect of development of manufacturing, technical and economic factors. Mostly used are: higher alcohols, linear alkyl benzenes, oxyethylated alcohols, α-olefines. It should be noted that the choice of organic raw

materials is associated with the subsequent use of the obtained SAS in various sectors of industry and everyday life. SAS based on higher alcohols and alkyl benzenes are mostly used in detergents and foam forming formulations, SAS on the base of oxyethylated alcohols – in liquid detergents, SAS based on α-olefines are used for technical needs. It follows from the stated above that the active base of detergents and foam forming formulations is the mixture of SAS, usually in the form of separate components [8]. However, there are data [9] that the sulfatizing monoethanolamides derivatives of fatty acids (FA MEA) have high surface active properties. Unfortunately, the low degree of sulfation limits their widespread use. That is why the process of sulfation of FA MEA is performed in the sulfatizing solvent [10], that is, the mixture of organic matter is sulfated. This process is given much less attention to in the periodicals. However, this method allows obtaining high quality products. Thus, the process of sulfation of the mixtures of organic substances requires more detailed study to obtain SAS of high quality.

3. Aims and objectives of the research

The purpose of the research is to develop a process of sulfation of the mixtures of organic substances by gaseous sulphur trioxide, diluted by dried air to obtain surface active substances of high quality.

To achieve the set goal, the following tasks are to be solved:

– to examine regularities of the process of sulfation of the mixtures of organic substances and to establish dependency of the degree of sulfation and pastes chromaticity on the basic technological parameters;

– to explore physical and chemical characteristics of the reaction mass in the process of sulfation and suggest recommendations on the use of obtained surface active substances in the foam forming formulations.

4. Materials and methods of research into the process of sulfation

As a sulfatizing solvent we chose a mixture of the higher alcohol of fraction C_{12}–C_{14} with average molecular mass of 188 g/mol and the higher alcohol of fraction C_8–C_{10} with average molecular mass of 136 g/mol. The choice of higher alcohol is associated with the fact that the sulfating mass based on it is characterized by unique properties [11]; in particular, its viscosity has an extremum at the sulfating degree equal to 50 % and it decreases until reaching practically the final degree of sulfating. The choice of these fractions is due to their commercial availability. As FA MEA we selected monoethanolamide of fatty acids of coconut oil with average molecular mass of 280 g/mol. The mixture of these substances was sulfated with gaseous sulphur trioxide diluted by dried air. As was demonstrated above, such a sulfatizing agent is widely used in industrial practice.

The research was carried out at the laboratory installation, shown in Fig. 2.

The working order on the installation is as follows. A required amount of organic raw material was loaded into Reactor 1. The air cleaned at filter 4 entered compressor 5. The compressed air was then accumulated in receiver 6. From the receiver, the air was supplied to evaporator 3 through drier 9

and rotameter 10, liquid SO_3 from dispenser 11 was also fed there. Gas mixture from the evaporator followed through refrigerator 12 to reactor 1, where the interaction between SO_3 and organic raw material occurred. Temperature in the reactor was maintained by thermostat 2. Analysis of the reaction masses to determine qualitative indicators of the process was conducted according to the known techniques [12].
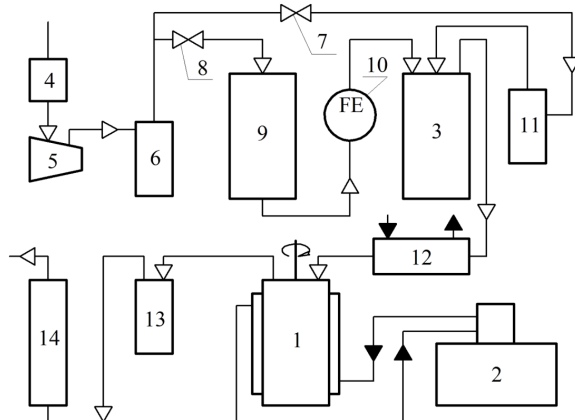

Fig. 2. Laboratory installation with a volumetric sulfation reactor: 1 — reactor; 2 — thermostat; 3 — evaporator; 4, 14 — filters; 5 — compressor; 6 — receiver; 7 — reducer; 8 — valve; 9 — drier; 10 — rotameter; 11 — feeder; 12 — refrigerator; 13 — absorber

5. Results of research into the process of sulfation

First, it was necessary to determine in which ratios the original components had to be taken. Analysis of previously conducted experimental research [10] revealed that the content of FA MEA in the mixtures of higher alcohols typically reaches 10 % of mass. There are no data available on the ratio of the selected fractions of higher alcohols. That is why we conducted experimental research into the ratio of higher alcohols of fractions C_{12}–C_{14} and fractions of C_8–C_{10}, respectively, 1–1÷4 and of the content of FA MEA of coconut oil equal to 10 % by weight of the total content of higher alcohols (Table 1).

The experiments were carried out at temperature of 313 K, molar ratio of the sulfatizing agent to the mixture of organic substances 1,1:1,0, concentration of sulfur trioxide in the gas air flow at 5 % by volume. Neutralization of the sulfating mass was performed by the aqueous solution of triethanolamine, 25 % by weight.

Table 1

Dependency of surface tension of SAS aqueous solutions on the ratio of higher alcohols of fractions C_{12}–C_{14} and fractions of C_8–C_{10} and the content of FA MEA equal to 10 % by weight

Ratio of higher alcohols of fractions C_{12}–C_{14} and of fractions C_8–C_{10}	Surface tension of SAS aqueous solution (0.5 % by weight, 323 K, distilled water, the Ross Miles method)
1:1	30,2
1:2	28,5
1:2,5	27,2
1:3	26,3
1:3,5	26,8
1:4	27,5

Next, we specify the content of FA MEA and dependency of surface tension of aqueous solutions of SAS on the content of FA MEA in the mixtures of higher alcohols at their ratio 1:3 without changing the conditions of the experiment (Tables 2, 3, respectively).

Table 2

Dependency of the degree of sulfating and pastes chromaticity on the content of FA MEA in the original product

Quality indicator	Content of FA MEA in the original product, % by weight						
	4	6	8	10	12	14	16
Degree of sulfation η, %	93,2	93,0	92,6	92,5	92,0	91,0	89,5
Pastes chromaticity, J, units by iodine scale	2	2	2	3	3	4	5

Table 3

Dependency of surface tension of aqueous solutions of SAS on the content of FA MEA in the original product

SAS concentration, % by weight	Content of FA MEA in the original product, % by weight						
	4	6	8	10	12	14	16
1	28,1	26,9	26,1	26,0	25,9	25,8	25,7
0,5	28,9	27,4	26,5	26,3	26,1	26,0	25,9
0,25	30,1	28,3	27,1	26,8	26,5	26,3	26,2
0,125	31,0	29,0	27,8	27,5	27,1	26,7	26,5
0,0163	34,8	30,6	28,8	28,4	27,8	27,3	26,9

As was indicated in [6], the main parameters affecting the quality of the obtained SAS are: molar ratio of the reagents, concentration of sulfur trioxide in gas air flow, temperature of the process of sulfating. Therefore, further experiments were conducted to determine dependencies of SAS quality on these particular parameters.

Fig. 3 demonstrates dependency of the degree of sulfation and pastes chromaticity on the molar ratio of reagents at T=313 K, concentration of SO_3 in the gas air flow is equal to 5 % by volume.
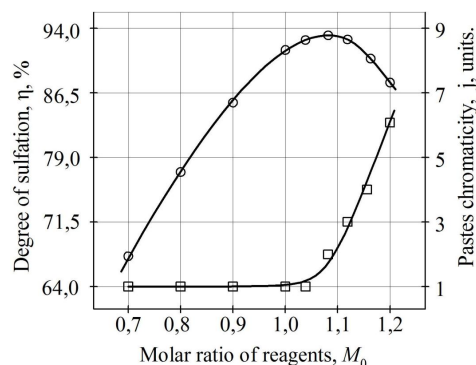

Fig. 3. Dependency of the degree of sulfation η and pastes chromaticity j on the molar ratio of reagents M_0

Dependency of the degree of sulfation and pastes chromaticity on the concentration of SO_3 in the gas air flow is presented in Table 4. Conditions of the experiment are as follows: molar ratio of reagents – 1,08:1,0, temperature of the process – 313 K.

Table 4

Dependency of the degree of sulfation and pastes chromaticity on the concentration of SO_3 in the gas air flow

Quality indicator	Concentration of SO_3, % by volume							
	2,5	3,0	3,5	4,0	4,5	5,0	5,5	6,0
Degree of sulfation η, %	93,3	93,3	93,2	93,2	93,1	92,9	92,6	92,0
Pastes chromaticity, j, units by iodine scale	2	2	2	2	2	2	3	4

Research into the influence of temperature on the quality of obtained SAS was performed at molar ratio: 1,08:1,0, concentration of sulfur trioxide in the gas air flow of 4.0 % by volume (Fig. 4).
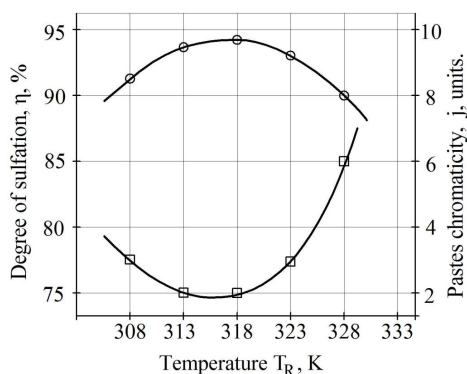

Fig. 4. Dependency of the degree of sulfation η and pastes chromaticity j on the temperature in reactor T_r

The research was conducted to determine the temperature of hardening of the reaction mass on molar ratio of the reagents (Table 5).

Table 5

Dependency of the temperature of hardening of the reaction mass on molar ratio of reagents

Molar ratio of reagents	0,2	0,4	0,5	0,6	0,7	0,9	1,0	1,1
Temperature of hardening, K	293	292	291	287	283	284	285	286

Dependency of the degree of sulfation and pastes chromaticity on alternating temperature regime is shown in Table 6.

Table 6

Dependency of the degree of sulfation and pastes chromaticity on alternating temperature regime (initial temperature 318 K)

Final temperature in reactor, K	Degree of sulfation, η, %	Pastes chromaticity, J, units
318	93,5	2
313	93,9	2
308	94,2	1
303	94,5	1
298	92,9	5

For mathematical modeling of the process of sulfation, it is necessary to have data on the change of magnitude of density and viscosity of the reaction masses during this process. The magnitude of density was measured by densimeter and the magnitude of viscosity – by the method of liquid outflow. The dependency of density of the reaction mass on the degree of sulfation and temperature is shown in Fig. 5.
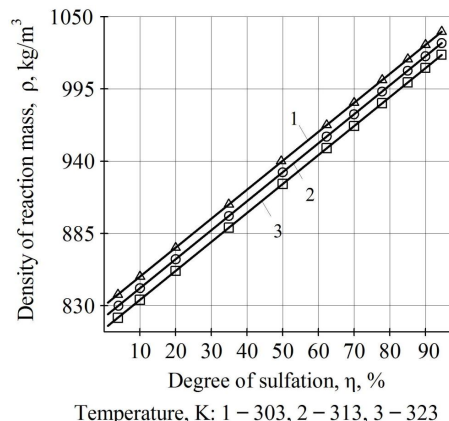

Fig. 5. Dependency of density of reaction mass ρ on the degree of sulfation η and temperature T

The dependency of dynamic viscosity on the degree of sulfation and temperature is shown in Fig. 6.
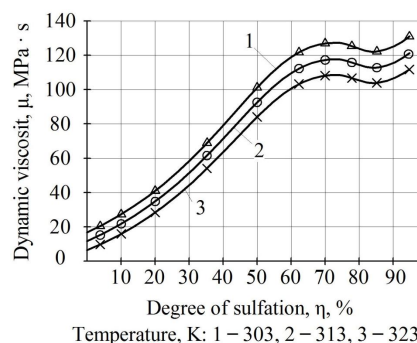

Fig. 6. Dependency of dynamic viscosity of the reaction mass η on the degree of sulfation μ and temperature T

We determined foam forming capacity of the received SAS compared with alkyl sulphates (Table 7).

Table 7

Foam forming capacity of received SAS

Concentration of SAS, % by weight	Foam height, mm		
	H_0	H_5	H_{10}
1,0	220	190	180
0,5	215	183	175
0,25	205	175	167
0,125	195	165	155

The initial height of the foam (H_0) for alkyl sulphates at concentration of 0.5 % by weight is 190 mm. The foam forming capacity was evaluated by the Ross-Miles method (temperature of 323 K, distilled water).

6. Discussion of results of the process of sulfation

As can be seen from Table 1, the surface tension of SAS aqueous solution as one of the indicators of SAS quality

reaches minimum level when the ratio of higher alcohols of fractions C_{12}–C_{14} and C_8–C_{10} equals 1:3.

As can be seen from Table 2, the content of FA MEA may be reduced down to 8 % by weight. It was found (Table 2) that the increase of the content of FA MEA in the original mixture exceeding 8 % by weight leads to lower degree of sulfation and to the growth in chromaticity of the obtained pastes. At the same time, we discovered dependency of the surface tension of aqueous solutions of SAS on the content of FA MEA (Table 3).

The data from Table 3 also confirm that the content of FA MEA may be reduced down to 8 % by weight. Table 3 also demonstrates that the reduction in the surface tension is particularly noticeable at low concentrations of SAS aqueous solutions.

Thus, the analysis of Tables 2, 3 displays that the content of FA MEA in the original organic product must be maintained at the level of 8 % by weight.

As can be seen from Fig. 3, at molar ratio of reagents 1,08:1, the maximum degree of sulfation is achieved with a slight increase in the pastes chromaticity. Analysis of the results of qualitative indicators of neutralized pastes revealed that the concentration of SO_3 in the gas air flow must be maintained within 3.5–4.5 % by volume (Table 4).

Fig. 4 shows that the dependency of the degree of sulfation and pastes chromaticity on the temperature in reactor has extreme character. With a decrease in temperature to 308 K, the degree of sulfation reduces while pastes chromaticity increases, due to the increased viscosity of the reaction mass. With the rise in temperature to 328 K, the pastes' quality also deteriorates, which is probably due to the increased speed in the course of adverse reactions. Taking into account the data from Fig. 4, the recommended temperature is 318 K.

As can be seen from Table 5, in contrast to all other SAS, the temperature of hardening of the reaction mass based on a mixture of organic substances that include FA MEA has extreme character; even at the molar ratio 1,1:1,0, the hardening point is reduced by 5–7 K. The data make it possible to gradually reduce temperature of the process after molar ratio of reagents >0.5:1.0.

As can be seen from Table 6, the final temperature of the process of sulfation may be reduced down to 303 K.

Fig. 5 demonstrates that the dependency of density of the reaction mass on the degree of sulfation and temperature is linear. By processing experimental data with the method of least squares, we obtained the following equation

$$\rho = 854 + 2,25 \cdot \eta - 9 \cdot (T-273). \qquad (5)$$

Error of calculation by equation (5) is 6 %.

As can be seen from Fig. 6, the dependency of dynamic viscosity of the reaction mass μ on the degree of sulfation η and temperature T has a maximum at η=72 % and a minimum at η=85 %, due to the nature of the change in viscosity of individual components. The processing of experimental data with the method of least squares using the Matlab software package enabled us to obtain the following equations:

$$\mu = 131 \cdot \exp[-0,5[0,0002 \cdot (T-273)^2 + +0,0009 \cdot \eta^2]] \text{ at } 0<\eta<72, \qquad (6)$$

$$\mu = 595,6 - 11,34 \cdot \eta + 0,07 \cdot \eta^2 + +0,1 \cdot (T-273) - 0,01 \cdot (T-273)^2 \text{ at } 72<\eta<94,5. \qquad (7)$$

Error of calculations by these equations is 8 %.

As can be seen from Table 7, the foam height increases ~ by 10 %, compared to pure alkyl sulphates, with sufficient foam stability in 5 min. and after 10 min.

The benefits of such research are obtaining new SAS from industrial fractions of organic substances that will find wide application in foam forming formulations. The shortcoming of the study is the degree of sulfation (η<95 %) that is not large enough, which is associated with the use of a volumetric reactor. Further research may be carried out to improve the process of sulfation of the mixtures of organic substances in the film reactor that makes it possible to increase the degree of sulfation up to 97–98 % and thus improve the issue of resource-saving of the original substance.

7. Conclusions

1. We examined regularities of the process of sulfation of the mixtures of organic substances, based on which we established dependencies of the degree of sulfation and pastes chromaticity on the basic technological parameters for obtaining surface active substances of high quality. Thus, at molar ratio of reagents 1.08:1, the maximum degree of sulfation is achieved with a slight increase in pastes chromaticity. It was demonstrated that the concentration of SO_3 in the gas air flow must be maintained within 3.5–4.5 % by volume, the recommended temperature of the process is 318 K with a gradual decrease to 303 K.

2. We determined dependencies of physic-chemical parameters of the reaction mass in the process of sulfation, which is necessary for mathematical modeling of this process. It was found that dependency of the density ρ on the degree of sulfation η has the form of a linear regression equation, and dependency of the viscosity μ on the degree of sulfation is described by exponential equation at $0<\eta<72$ and the equation of second order at $72<\eta<94,5$. The coefficients in these equations are obtained by the method of least squares.

3. SAS of such quality may be used in the foam forming formulations, for example, for fire extinguishing, for isolation of surfaces of toxic liquids, and for dust suppression.

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