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Studying the Patterns of Alkylbenzosulfonic Acid Color Change using Computer Modeling System

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Abstract

Within the framework of the work, a mathematical model of the process of sulfonation of linear alkylbenzenes with SO_3, which takes place in a multitube film reactor, is described. The causes and regularities of changes in the most important indicator of the quality of alkylbenzenesulfonic acid - its color index - are described. Using a mathematical model, it was found that the content of light aromatic compounds in the sulfonation feedstock worsens the color of ABS and leads to a reduction in the duration of the interwashing cycle.

Keywords: *Sulfonation; Linear alkylbenzene; Alkylbenzenesulfonic acid; Multi-tube film reactor; Process mode violation; Mathematical modeling.*

1. Introduction

Recently, significant efforts have been made to develop surfactants to be used in the detergent industry. In commercial use, some of the surfactants such as α-sulfomethyl esters and alkyl polyglucosides are known as novel materials. Some other materials such as ethoxylated amines, alkanolamides, betaines, alkyl diphenyls and oxydisulfonates have been regularly used in other industries for many years. The most commonly used surfactants used by the industry in detergent powders are linear alkylbenzene sulfonates. This surfactant is an inexpensive and readily available ingredient that is effective for removing dirt, but less so for greasy or oily stains [1-4].

Despite the variety of detergent compositions, the features of the surfactant molecular structure are determined by two main properties: adsorption from the bulk of the solution on the phase interface and the formation of large aggregates (micelles) in the solution. Due to these properties, surfactants find application in almost all industries, agriculture, transport and are used in solving environmental problems.

To date, three groups of industries can be distinguished, the development of which is closely related to the use of surfactants. The first group should include industries in which these products are used for a long time, and in the near future it is necessary to significantly expand the range of surfactants and improve their quality indicators. First of all, these are various types of synthetic detergents, pharmaceutical and cosmetic preparations, textile auxiliaries, emulsifiers for the production of polymerization resins, rubbers, and latexes. The second group includes industries related to the fuel and energy complex (extraction, primary processing and transportation of oil and gas, coal industry), machine-building complex (technical detergents for various purposes, conservation lubricants, cutting fluids, etc.), as well as the chemical-forest complex (production of cellulose, paper and paper products). The third group includes fast-growing and knowledge-intensive industries, such as biotechnology, electronics, biological protection of animals and plants [4].

The first detergents were soaps made from naturally occurring substances. However, fatty soaps have some disadvantages. Their washing action is manifested only in an alkaline environment; with calcium and magnesium salts contained in hard water, they form sticky insoluble salts that settle on tissues and contaminate them. Alkalis contained in soap weaken the strength of woolen and silk fabrics, as well as fabrics made of polyester fibers, especially at elevated temperatures, and can also change the color of fabrics. In addition, fatty raw materials for soaps are a scarce food product. All this determines the relevance of the development of production and use of synthetic detergents. The most important task facing the industry (along with the increase in the production of surfactants and detergents) is the expansion of the range and quality of detergents, the growth of economic efficiency and environmental friendliness of production. The decisive role here belongs to the search for new and modification of existing surfactants and detergents, as well as compositions, mainly in the form of liquids and pastes, the creation of effective processes for their synthesis, and the development of ways to fundamentally improve and reconstruct existing industries [5].

As surfactants, alkylbenzenesulfonates (ABSA), which have thermal stability, non-hygroscopicity, and good colloidal chemical properties, are most widely used. Available raw materials are used for their production. They are the cheapest and best ingredients in synthetic detergents [6]. Fig. 1 shows a process flow diagram for the production of ABSA, implemented at one of the Russian enterprises. According to this technology, ABSA manufacturing technology consists of several technology-related processes: dehydrogenation of alkanes on Pt-catalyst with alkenes obtaining; hydrogenation of by-product (dienes); alkylation of benzene with obtaining of linear alkylbenzenes (LAB) using HF as catalyst; sulphonation of LAB by SO_3 with obtaining of ABSA.

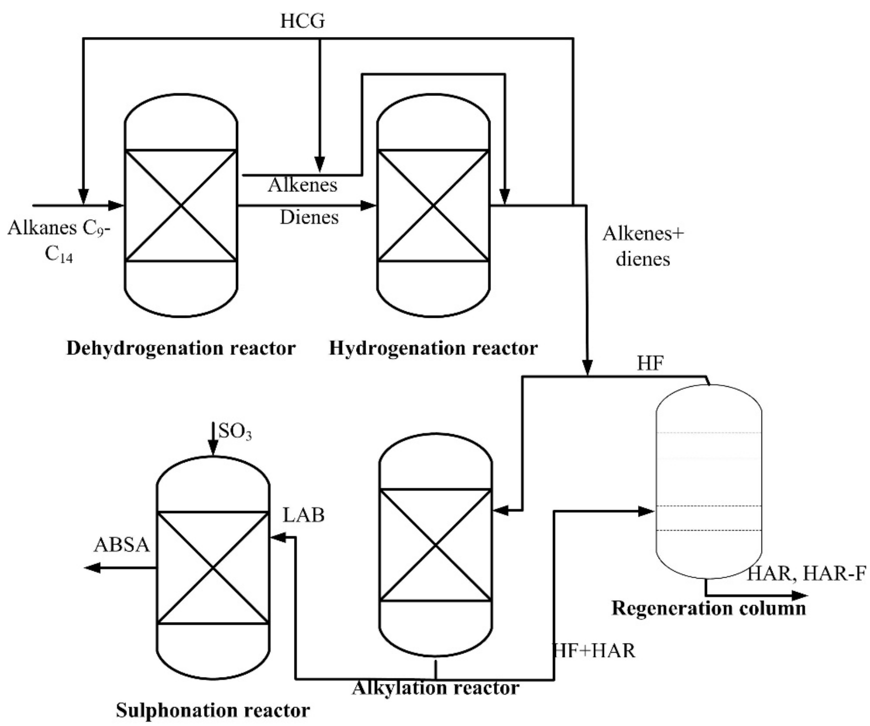


Figure 1. Alkylbenzenesulfonic acid manufacturing complex

The most important quality indicators of ABSA are its ratio in the product flow, as well as color. In previous works [7–9], the influence of technological parameters on the production of ABSA was considered using a mathematical model of the sulfonation process. According to literary sources, the deterioration of the color index of ABSA occurs during aging as a result of LAB oversulfonation reactions, as well as a result of the formation of color-forming components directly in the sulfonation reactor [10–12]. This work is devoted to the study of the patterns of change in the color of ABSA.

2. Mathematical model of sulfonation process

Mathematical models and computer simulators are affective in industrial processes optimization [13–15]. Reaction networks and the kinetic models of the processes have been developed and presented in [7].

In the stationary regime change in *i*-th hydrocarbon concentration with reactor volume (contact time) the plug flow reactor model can be written as follows:

$$\frac{dC_i}{d\tau} = W_i \quad (1)$$

Assumption of ideal displacement regime in alkylation reactor was confirmed by calculation of Peclet criterion (403.7>200).

According to experimental data, characteristics of benzene alkylation reactor are similar to adiabatic. Then the heat balance equation in steady state can be written as follows:

$$\rho C_p \frac{dT}{d\tau} = \pm \sum_{j=1}^{N} (-\Delta H_j) W_j \quad (2)$$

Mathematical models of alkylation and sulphonation processes also give a good convergence of experimental and calculated data. Thus, the developed computer programs are suitable for the refinery processes monitoring and optimization.

After considering the influence of the diffusion component, the mathematical model of the sulfonation process takes the following form:

$$\left(\frac{\partial C}{\partial t}\right)_R = D_R \left(\frac{\partial^2 C}{\partial R^2}\right) + \frac{1}{R}\frac{\partial}{\partial R} \quad (3)$$

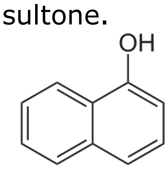
where D_r is the diffusion coefficient of gas into liquid; R –radius of the reactor tube, m.

3. Results and discussion

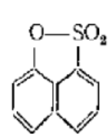
The color of ABSA depends on their chemical composition, the degree of sulfonation, as well as on the production and purification processes. Usually, ABSA is a mixture of different isomers and homologues, which can have different colors depending on their chemical structure. For example, anionic ABSA containing longer side chains often have a darker color than shorter side chains. In addition, during the production of ABSA, impurities can be formed, which can also affect the color of the product. However, in general, ABSA have a relatively low color, which makes them suitable for use in various industrial and domestic applications, including the manufacture of detergents, cosmetics, washing powders, etc.

Pure ABSA without non-sulfonated residue and other impurities has an amaranth color (red-pink). The table lists the characteristics of the main substances that make up the reaction mixture of the LAB sulfonation reactor [16].

Pure ABSA without unsulfonated matter and other impurities has an amaranth color (red-pink). The red-pink color of pure ABS is due to the presence of: - Naphthol-6-sulfonic acid (red-brown); - Nitro-4 (4-nitroaniline-azobenzene-4-sulfonic acids) (red diamonds) - Naphthylamine-4-sulfonic acids (red). These compounds are responsible for the color of red, oil-soluble sulfonic acids. After the latter are completely freed from these sulfonic acids, red sulfonic acids lose their reddish color and acquire their characteristic light-yellow color, which gradually turns dark brown, apparently due to the oxidation of free sulfonic acids by atmospheric oxygen [17]. Naphthols are hydroxy derivatives of naphthalene During sulfonation of naphthols, naphthol-sulfonic acid (red) is formed, which easily releases water, forms an ester-sultone.



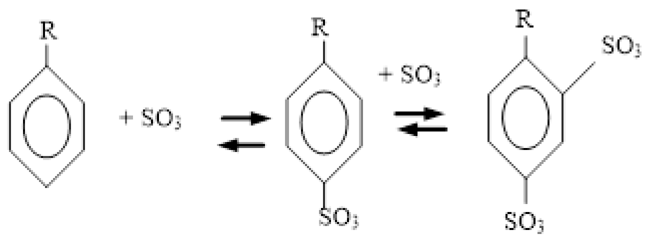
naphthols



naphtol sulphonic acid

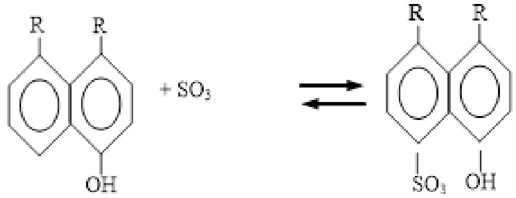
The acid acquires a light-yellow color (fresh acid). Further, free ABSA is oxidized by atmospheric oxygen, as a result of which the acid darkens. The oxidation reaction is exothermic, so it intensifies with decreasing temperature. Color can be restored by exposure to a protic reducing agent such as hydrogen peroxide. Thus, the following reasons for the darkening of ABS can be distinguished:

- ABSA resulfonation reactions in excess of SO_3 with formation of disulfonic acids (reaction 1).

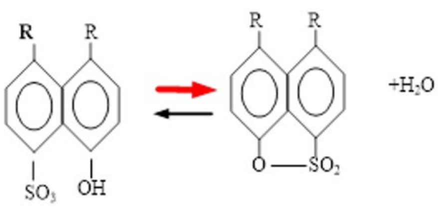


(1)

- ABSA oxidation reactions, as a result of which the equilibrium of the dehydration reaction of naphthol-sulfonic acid is disturbed.



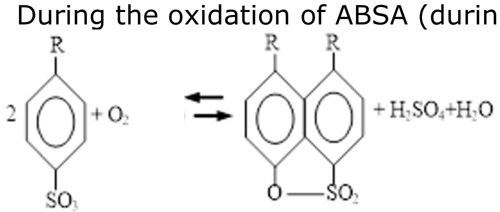
(2)



(3)

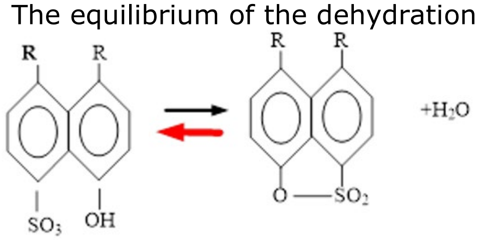
To maintain a stable light color of ABSA, the equilibrium of the dehydration reaction of naphthol-sulfonic acid must be shifted to the right (reaction 2).

During the oxidation of ABSA (during aging), an additional amount of sultones is formed:



(4)

The equilibrium of the dehydration reaction shifts to the left:



(5)

The presence of rich yellow sultones and red-brown naphthol-sulfonic acid in the mixture leads to the acquisition of brown ABSA. In addition, during aging, sulfonation of ABSA and AB, which are part of the non-sulfonated residue, contained in the product mixture with sulfuric acid and pyrosulfonic acid, occurs, the content of unreacted AB in the acid decreases. Due to its exothermicity, the reaction intensifies with decreasing temperature, so when the acid is stored at low temperatures, it darkens faster. Moreno [18] notes that sulfones, in contrast to unreacted AB, practically pass into the target product during the aging of ABSA, therefore it is advisable to maintain less severe conditions for the SO_3/LAB ratio, subsequently increasing the aging time [17, 19].

Table 1. Aggregate state and properties of the components of the reaction mixture of the AB sulfonation reactor

Substance	Aggregate state at T - 308 K, P - 0.04 MPa	Color
ABSA	viscous liquid	From light dark brown to blackish in color depending on the brand. Anhydrous free sulfonic acids, sufficiently purified from other sulfonic acids and non-sulfonated compounds, as well as their anhydrous solutions, are colored amaranth (pink).
disulfonic acids	viscous liquid	brown
H_2SO_4	liquid	colorless
sulfones	crystals	colorless
pyrosulfonic acid	liquid	colorless
ABSA anhydride	liquid	colorless
ethers	liquid	colorless
sulfate alcohols	liquid	colorless
sultones	liquid	yellow

Thus, during aging, unreacted AB passes into the target product, as well as into disulfonic acids, resulting in darkening of the acid and a decrease in its commercial properties. It is not possible to model the dynamics of color change in the framework of this work due to the small number of components that cause darkening of the acid, as well as the lack of experimental data on their content. However, it is obvious that the viscosity of the reaction medium affects the color of ABSA: with an increase in the viscosity of the reaction medium, a violation of the uniformity of sulfonation is observed, and AB oversulfurization occurs in the upper layers. Also, the viscosity of a substance can affects its color in the sense that it can change the ability of a substance to absorb light of different wavelengths. If the viscosity of a substance is high, then its molecules can be more densely packed, which can lead to a change in its optical properties and color [20-21]. In other words, there is a dependence of the color of ABSK on the amount of light aromatic compounds that have passed through the sulfonation reactor during the interwashing period (Table 2).

With a large amount of light aromatic compounds that have passed through the reactor during the interwashing period, a sharp increase in the rate of color change is observed (in accordance with the rate of increase in viscosity).

Example

Period: 51.2 tons of light aromatics - 12 days - an increase in color by 6 Klett units;

Period: 112.7 tons of aromatics - 11 days - an increase in color by 41 Klett units.

With an increase in the amount of light aromatic compounds that have passed through the sulfonation reactor, the rate of change in the color of ABSA also increases. In this case, the color value at the end of the interwash period depends on its initial value. In some interwash periods, the color value of ABSK up to 52 units is achieved. Klett, the amount of aromatics that passed through the sulfonation reactor during the interflushing period is about 112 tons. A sharp increase in the color of ABSA at the end of the interwashing period can be explained by the accumulation of high-viscosity components of the mixture in the reaction film due to an increase in the contact time of the reagents and an increase in the acidity of the medium (the concentration of sulfones increases).

Table 2. The dynamics of the change in the color of ABSA and the duration of the interwashing period depending on the amount of light aromatic compounds that have passed through the sulfonation reactor

Interwashing period			Amount of light aromatic compounds passed through the sulfonation reactor during the interwashing period, t. (experiment)	Color, Klett units (experiment)	
				At the beginning of the period	At the end of the period
1	start	08.01. 2021	51,8	10	22
	end	16.01. 2021			
2	start	04.03. 2021	56,7	11	20
	end	11.03. 2021			
3	start	06.04. 2021	51,2	10	16
	end	18.04. 2021			
4	start	29.12. 2021	47,1	9	13
	end	05.01. 2021			
5	start	03.07. 2021	112,7	11	52
	end	14.07. 2021			
6	start	07.08. 2021	107,4	11	39
	end	21.08. 2021			
7	start	08.04. 2022	34,5	10	15
	end	14.04. 2022			
8	start	14.04. 2022	57,6	10	12
	end	23.04. 2022			
9	start	21.06. 2022	53,5	10	17
	end	01.07. 2022			

4. Conclusions

In this research, a mathematical model of the LAB sulfonation process was developed with due consideration of the reaction medium deactivation by highly viscos components, diffusion and mass transfer. This model considers the relationship with the mathematical model of the previous stages of the ABSA production, is sensitive to changes in the feedstock composition and has a high predictive potential.

To maintain a stable light color of ABSA, the equilibrium of the dehydration reaction of naphthol-sulfonic acid must be shifted to the right. During the oxidation of ABSA, an additional amount of sultones is formed. The presence of rich yellow sultones and red-brown naphthol-sulfonic acid in the mixture leads to the acquisition of brown ABSA. Optimization of the sulfonation process consists in regulating the equilibrium of the reaction of dehydration of naphthol-sulfonic acid and oxidation of ABSA. There is a clear correlation between the ratio of the proportions of light aromatics and the color of ABSK, in addition, the duration of the interwashing cycle plays a role.

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