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STUDYING THE PROCESS OF PHENOL SULFOMETHYLATION IN THE TECHNOLOGY OF WATER SOLUBLE SURFACTANTS

Об'єктом дослідження є реакції сульфометилювання фенолу у водному середовищі, з метою отримання водорозчинних нетоксичних продуктів на його основі, що використовуються в якості поверхнево-активних речовин (ПАР). Одним з найбільш проблемних місць є необхідність підтримки стабільності системи і утримання заданого pH при введенні сульфуючого агента: температура реакції 125–130 °С, час поліконденсації 8 годин, реакція проходить під тиском. Цим методом отримують продукт реакції, який є досить складною сумішшю мономерів, димарів, тримерів і вільного фенолу. Також, при проведені реакції сульфометилювання фенолу у водному середовищі утворюється реакційна маса, яка являє собою двофазну систему: верхній органічний шар – феноли, нижній шар – водний розчин бісульфітного похідного формальдегіду. Суттєвими недоліками цього способу є відносно низький вихід цільового продукту та висока температура проведення реакції. В ході дослідження проводилось вивчення реакції сульфометилювання фенолу в умовах міцелярного каталізу. Визначено оптимальну кількість вихідних речовин і кількість міжфазного каталізатору. Застосування цих каталізаторів дозволило поліпшити основні технологічні параметри: знизити температуру реакції з 125–130 °С до 75–80 °С, скоротити тривалість процесу до 1 години, проводити процес при атмосферному тиску. Перевагою даної технології також є безвідхідне, одностадійне виробництво та доступна українська сировина. У ході дослідження отримано продукт, який має властивості, характерні для ПАР: при збільшенні молекулярної маси поверхневий натяг водних розчинів підвищується та призводить до зниження поверхневої активності. Таким чином, за результатами досліджень технологічних характеристик отриманих зразків ПАР можна запропонувати використання їх в якості аніоноактивних ПАР, що застосовуються як стабілізатори у виробництві органічних барвників, текстильно-допоміжних речовин та як пластифікатори для бетону.

Ключові слова: *сульфометилювання фенолу, фенолальдегідна смола (новолак), бісульфіт натрію, міжфазний каталіз, поверхнево-активні речовини.*

1. Introduction

The study of the reaction of phenol sulfomethylation is of practical interest in connection with the availability of phenol and the possibility of synthesizing water-soluble non-toxic compounds on its basis, which are used as additives, bactericidal substances and additives to concrete mixtures. As well as dispersants, plasticizers, ion exchange resins, etc. [1, 2]. One of the studied methods for the synthesis of such compounds is the condensation of phenols with formaldehyde and the further sulfonation of the resulting phenol-aldehyde resin (Novolac) with sulfuric acid, taken in a small amount. The Novolac type resin is sulfonated at a temperature of 110–120 °C with concentrated sulfuric acid for 4–8 hours [3, 4]. The disadvantage of this method is that the reaction product is a rather complex mixture of monomers, dimers, trimmers and free phenol [5]. The production of water-soluble products by another method: phenol sulfomethylation, is carried out with bisulfite compounds of aldehydes. The product of the interaction of formaldehyde with sodium bisulfite, due to its low price, is of great interest in using it as an agent for sulfomethylation [6]. The authors in previous works [7, 8] conducted a study of the reaction of phenol sulfomethylation prepared in advance by a bisulfite derivative of formaldehyde in an aqueous medium at a molar ratio of formaldehyde: sodium bisulfite, equal to 1:1.25. To the mixture was added phenol and, with constant stirring, heated to 125–130 °C under pressure. The reaction mass was kept at this temperature for 1 hour. At the same time, the resulting reaction mass is a two-phase system: the distribution of phenol in the upper organic layer was noted, and the lower layer was an aqueous solution of the formaldehyde bisulfite derivative. The transition degree of reagents through the interface of the phases (IP) is low. Significant disadvantages of this method are the relatively low yield of the target product and the relatively high temperature of the reaction. Therefore, the authors consider it important to use the method of stabilization of the reaction mass under interfacial catalysis using surfactants as a catalyst (interfacial catalysis – IFC) [9].

So, *the object of research* is the reaction of phenol sulfomethylation, with the aim of obtaining water-soluble non-toxic products based on it used as surfactants. And *the aim of research* is studying the possibility of carrying out the phenol sulfomethylation reaction with bisulfite derivative of formaldehyde in an aqueous medium in the presence of interfacial catalysts and the selection of optimal technological conditions for producing surfactants based on them.

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2. Methods of research

Under laboratory conditions, a series of reactions of phenol sulfomethylation were carried out in the presence of various surfactants: non-ionic surfactant Neonol AF-9-12 (monoalkylphenol oxyethylation) and anion-active surfactats of NF dispersants (the product obtained by sulfonating naphthalene with sulfuric acid followed by condensation with formaldehyde). To stabilize the pH of the system, diethanolamine was used in a volume of 0.05 % of the total mass of the main components. The amount of catalyst was taken at the rate of 0.1; 0.05; 0.005 % of the mass of the feed.

Experiment 1. In a three-neck round-bottomed flask with a capacity of 1.5 dm^3 was charged 429 g of 94 % sodium sulfite, 240 ml of water, 190 g of phenol, 204 g of formalin (37 % formaldehyde solution), 1.06 g of Neonol AF-9-12 and 5.3 g of diethanolamine. The reaction mass is heated to 75–80 °C with constant stirring. It is kept at this temperature for 1 hour. (In this case, the reaction mass can self-heat up to 85–90 °C). The mass is cooled and sampled for analysis. The finished product is a viscous orange liquid.

Experiment 2. Conducted by analogy of experiment 1. The amount of catalyst for Neonols AF-9-12 loaded 0.53 g

Experiment 3. Conducted by analogy of experiment 1. The amount of catalyst for Neonols AF-9-12 loaded 0.053 g

Experiment 4. In a three-necked round-bottom flask with a capacity of 1.5 dm^3 load 429 g of 94 % sodium sulfite, 240 ml of water, 190 g of phenol, 204 g of formalin (37 % formaldehyde solution), 1.06 g of dispersant NF, as well as 5, 3 g of diethanolamine. The reaction mass is heated to 75–80 °C with constant stirring. The reaction mass is maintained at this temperature for 1 hours with constant stirring. The mass is cooled and sampled for analysis. The finished product is a viscous liquid of reddish-brown color.

Experiment 5. Conducted by analogy of experiment 4. The amount of catalyst dispersers NF loaded 0.53 g

Experiment 6. Conducted by analogy of experiment 4. The amount of catalyst dispersers NF loaded 0.053,

Analysis of the products was carried out in accordance with regulatory documents [10].

Due to the fact that the obtained products are polymolecular, in research their composition was characterized by the *K* value (the ratio of the content of high and low molecular weight fractions).

The degree of sulfonation was determined by the content of organic sulfur and expressed by the number of sulfo group (*S* value) per 1000 molecular weight units.

According to the characteristic of the surface-active properties of the samples, the critical micelle concentration (CMC) was determined, which was determined by the properties of the solution, depending on the number and size of the kinetically active particles, depending on its optical characteristics.

3. Research results and discussion

The properties of the obtained products were compared with anion-active surfactant, known as IP dispersant, which is a condensation product of phenol, formaldehyde and sodium sulfite. The obtained data are presented in Table 1.

As a result of the research, it is found that Neonol AF-9-12 and NF dispersant have a strong influence, activates the process of phenol sulfomethylation. Reactions proceed with a fairly high speed at a temperature of 75–80 °C in an alkaline medium (pH).

Table 1

Physical and chemical indicators of the obtained products

No.	Product	Mass fraction of sodium sulfate, %	Mass fraction of water-soluble substances, %	Water pH	*K*	Sulfonation degree (S)	CMC, g/dm^3
1	IP dispersant	0.1	0.1	–	1.1	2.0	2.0
2	The product of phenol sulfomethylation in the presence of Neonol AF-9-12:						
	Experiment 1	0.15	0.1	8	0.5	1	2.5
	Experiment 2	0.3	0.2	8	1	1.5	3.5
	Experiment 3	0.25	0.15	9	0.5	1.6	2.4
3	The product of phenol sulfomethylation in the presence of NF dispersant:						
	Experiment 4	0.15	0.1	9	1	1.5	3.6
	Experiment 5	0.23	0.2	8	1.5	2.0	4.1
	Experiment 6	0.2	0.15	9	1.5	2.1	3.7

The most important characteristic of surfactant is the critical micelle concentration (CMC). CMC is the minimum molar concentration of surfactant at which one can experimentally detect a colloid-dispersed phase.

At low concentrations ($<10^4$ mol/l), surfactant form true solutions, and with increasing concentration, micelles appear in them, formed as aggregates of a special structure.

As can be seen from the Table 1, CMC of the obtained products is close in value to the CMC of the sample for comparison.

Also, with an increase in *K*, the value of CMC increases, thus with increasing molecular weight, the surface tension of aqueous solutions increases and leads to a decrease in surface activity. Thus, the largest CMC can be assumed that the resulting products can be used as surfactants.

Based on a study of toxic and hygienic properties, it is found that the resulting product based on sulfomethyl phenol-formaldehyde belongs to the third class of hazard. Therefore, the obtained products can be proposed for use as anionic suractant in various applications: in the textile industry as auxiliary substances (stabilizers, wetting agents, dispersants), in construction (plasticizers for concrete), etc.

4. Conclusions

As a result of research, a method is proposed for producing anion-active surfactant, which includes phenol sulfomethylation of bisulfite derivatives of formaldehyde at a temperature of 75–80 °C under micellar catalysis conditions. Oxyethylated monoalkylphenol based on propylene trimers (non-ionic surfactant Neonol AF-9-12) and the product obtained by sulfonating naphthalene with sulfuric acid followed by condensation with formalde-

hyde (anion-active surfactant – NF dispergator) is used as a catalyst. Diethanolamine is recommended to stabilize the pH of the system. It has been established that the addition of AF-9-12 as Neonol catalyst or NF dispersant in an amount of 0.1–0.005 % of the total mass of reagents makes it possible to obtain a homogeneous and stable in time reaction mass. The use of these catalysts makes it possible to improve the main technological parameters: reduce the reaction temperature from 125–130 °C to 75–80 °C, shorten the process time from 3 hours to 1 hour, carry out the process at atmospheric pressure. The advantage of this technology is also non-waste, single-stage production and is available to Ukrainian raw materials.

According to the research results, a technology for the production of surfactants is developed, which is environmentally friendly and cost-effective, and can be offered to expand the scope of surfactants and is an alternative substitute for substances already used.

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