Synthesis of Polyoxyalkylene Glycol-ether Active Bases for Demulsifying Compounds

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Abstract. Today, the development of the company's oil and gas assets is complicated by the extraction of products with a high proportion of waterlogging, due to the long history of operation of most fields. When oil and reservoir water move through pipelines and the borehole and mix them together, crushing occurs (this process is called dispersion), resulting in the formation of water-oil emulsions. An emulsion is a mixture of two mutually insoluble liquids, one of which is dispersed in the other in the form of small droplets (globules).
To date, the main methods of combating the formation of water-oil emulsions (VNE), which complicate the production process, is the supply of demulsifying reagents [1]. For effective operation, demulsifiers must have a set of properties, the most important of which is demulsifying activity. However, the currently used demulsifiers have a dosage limit at which the EE is destroyed during transportation, but an intermediate layer accumulates in the oil treatment plant (UPN), reservoirs, which leads to disruption of the oil treatment process in the technological chain "extraction – transportation - processing", which significantly affects the quality of commercial oil and its cost price.
Thus, the creation of new demulsifying compositions to increase the efficiency of the decomposition process of stable water-oil emulsions remains relevant.
This article describes a method for developing polyoxyalkylene glycol ether additives for demulsifier compositions by a multifactorial experiment and determining the optimal ratios of the initial raw materials used in synthesis, as well as a method for evaluating the demulsifying activity of the obtained compositions in laboratory conditions.

Keywords: surfactants, demulsifier composition, active base of demulsifier, demulsifier, mathematical modeling, 3-factor experiment.

1. Introduction

The oil and gas industry is one of the most important sectors of the Russian economy. 2023 marked the 80th anniversary of the beginning of the development of oil fields in the Republic of Tatarstan. The intensification of production over such an impressive period of time has led to the problem of waterlogging of deposits, which complicates the production process as a result of the formation of water-oil emulsions. Currently, the average water content of Tatneft's fields is about 86 percent [1]. One of the ways

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to eliminate the consequences of this problem is effective tubular demulsification of the VNE [2], [3], [4].

The purpose of the work: to develop polyoxyalkylene glycol-ether active bases for the composition of demulsifiers by a multifactorial experiment and achieve optimal formulations that will have a higher rate of water separation and reduce the formation of an intermediate layer.

2. The experimental part

The synthesis is based on the interaction of a dibasic carboxylic acid with an alkoxylated simple polyester and the production of polyoxyalkylene glycol-ester active bases with different chain lengths. Polyoxyalkylene glycol-ether active bases with different chain lengths were obtained by reacting dibasic carboxylic acid (succinic, adipic, or oxalic) with alkoxylated simple polyester in the presence of a catalyst (P_2O_5) at a temperature of 160-190 °C for 4 hours with distillate distillation (Fig.1). The synthesis design was developed using mathematical planning of a multifactorial experiment. This method is a choice of the number of experiments and their conditions that meet the specified requirements, which helps to take into account the influence of various variables on the process under study and optimize the allocation of resources to achieve the desired result. This is a method of purposeful experimentation carried out in conditions of incomplete knowledge of the mechanism of influence of various factors on the process [5]. For this purpose, the minimum and maximum permissible ratios of the components were established (Table 1) based on their stoichiometric ratios during chemical reactions.

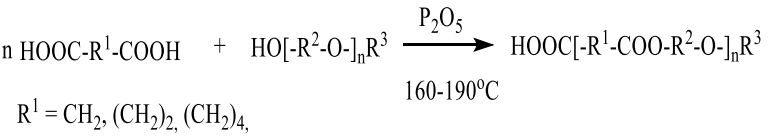

Fig. 1. The Scheme of the reaction.

Table 1. The minimum and maximum permissible ratios of the components.

Component	Minimum value, %	Maximum value, %
Alkoxylated PP	88	97
Dicarboxylic acid	0	13
APAV	0	7
Alkoxylated PP	88	97
Dicarboxylic acid	0	13

According to the given ratios, a ternary diagram was constructed (Fig. 2) showing the area of various optimal concentrations of components. Thus, 9 individual formulations were obtained, which will allow us to determine the most optimal search area for formulations (Table 2).

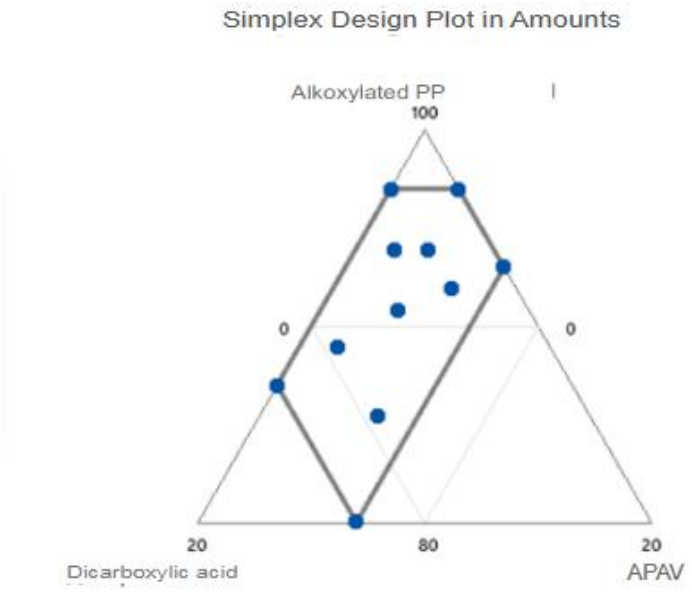

Fig. 2. Simplex graphic design of an experiment based on the ratios of three components.

Table 2. Optimal search area for formulations.

Name	Alkoxylated PP	Dicarboxylic Acid
SDE -1	91,9%	2,9%
SDE -2	90,8%	5,8%
SDE -3	88,9%	9,4%
SDE -4	93,0%	0,0%
SDE -5	80,0%	13,0%
SDE -6	97,0%	0,0%
SDE -7	97,0%	3,0%
SDE -8	87,0%	13,0%
SDE -9	93,9%	2,9%
SDE -10	85,4%	9,4%
SDE -11	93,9%	4,4%

3. Synthesis conditions

To carry out the synthesis, a round-bottomed three-necked flask was used, equipped with a direct refrigerator, a top-mounted stirrer and a flask heating element with a thermal sensor. The required amount of alkoxylated polyester was heated to 60 ° C in a reactor and dibasic carboxylic acid was added in portions with constant stirring. Next, the reaction mass was brought to 165 ° C, the holding time was 4 hours with distillate distillation. After that, the semi-finished product was cooled to 60 ° C and APAV was added until completely mixed and cooled. The synthesis was controlled through the determination of the acid number, which decreased.
Thus, 11 amber-colored intermediates were obtained, on the basis of which 5 compositions of demulsifiers were made (Table 3) in combination with a solvent mixture and a basic polyester base, unstable compounds are not included in the table.

Table 3. Compositions of demulsifiers.

Components	Composition №1	Composition №2	Composition №3	Composition №4	Composition №5
Solvent mixture	58,38	59,38	57,62	54,99	9,77
Basic polyester base	28,28	25,63	24,28	25,43	26,33
SDE -3	13,34				
SDE -6		14,99			
SDE -7			18,51		
SDE -8				19,58	
SDE -9					13,9

The demulsifying activity of the obtained compositions was evaluated in the laboratory using the "bottle test" method on an artificial emulsion.

This method makes it possible to evaluate the following parameters in the field, which were taken into account as responses in a multifactorial experiment:

- the rate of separation of water from the emulsion into the free phase (the rate of destruction of the emulsion);
- the quality of the phase boundaries (the presence of an intermediate layer consisting of an undisturbed emulsion and its thickness);
- residual water content in the settled oil.

It should be noted that in laboratory conditions it is impossible to ensure the same intensive mixing of the demulsifier in the emulsion as in real systems and achieve a similar reagent efficiency. Therefore, the dosages of demulsifiers used in laboratory studies are always higher, usually 2-5 times higher than in real systems [7].

4. The essence of the "bottle test" method

The emulsion is poured into 100 ml settling tanks, taken according to the number of reagents being tested. The reagent is dispensed with a micro-syringe. After adding the demulsifier to the emulsion, all the settling tanks are shaken (50-100 times) and set for thermostating at 60 ° C. After the specified time intervals, the results are recorded and entered in the table. From the settling tanks in which the results are recorded, oil samples are taken from the upper layer to determine the residual water by centrifugation. Test results (Table 4) The new compositions from Table 3 were compared with the reference sample of the demulsifier. Based on the data obtained, a graph of the dependence of water separation on time is constructed (Fig. 3).

Table 4. Test results.

Composition №/time	15 minutes	30 minutes	45 minutes	60 minutes	Residual water,	The industrial layer
1	87%	91%	93%	93%	0,2%	0,02%
2	83%	87%	87%	91%	0,5%	0,2%
3	81%	87%	87%	87%	0,3%	0,2%
4	79%	83%	83%	85%	0,5%	0,4%
5	87%	95%	95%	95%	0,1%	0,02%
Reference DE	83%	85%	85%	85%	0,3%	0,6%
1	87%	91%	93%	93%	0,2%	0,02%

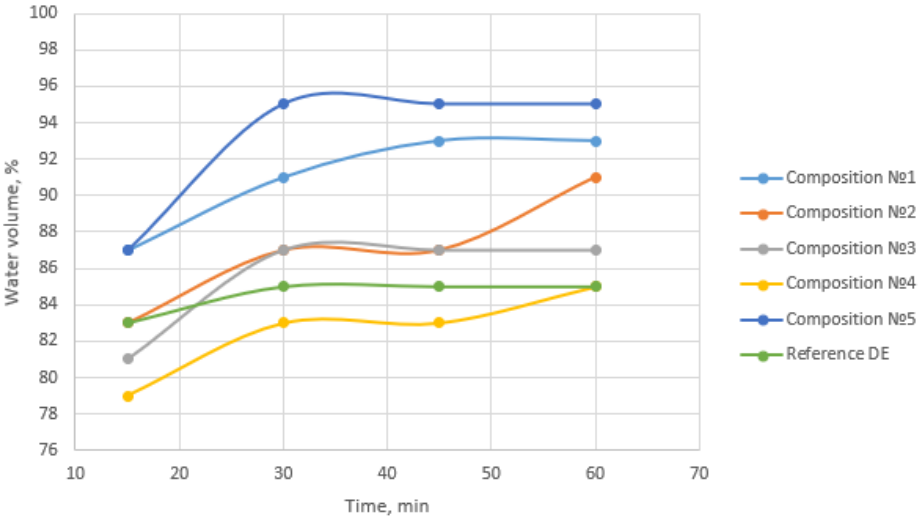

Fig. 3. Graph of the destruction of the VNE in time.

5. Discussion of the results

According to the data in Table 4 and Fig. 2, it was found that the new compositions demonstrate different demulsification efficiencies. Compositions 1 and 5 surpass the reference reagent in key parameters: the volume of separated water, the content of residual water in the oil, and the thickness of the resulting intermediate layer. At the same time, composition 1 is slightly inferior to composition 5 in terms of the rate of water separation, however, their indicators for residual water and the intermediate layer are identical. Compositions 2 and 3, although they provide a higher final water separation compared to the reference, form a larger volume of residual water and a more pronounced intermediate layer. Composition 4 and the reference demulsifier showed comparable effectiveness in terms of the degree of dehydration, however, according to secondary criteria (residual water and intermediate layer), the reference sample has an advantage. Presumably, the high efficiency of compositions 1 and 5 is due to the optimal combination of molecular weights and hydrophilic-lipophilic balance values for this oil system. The analysis of the kinetics of the process (Fig. 2) allowed us to identify three characteristic types of emulsion destruction. To the first type ("stepwise") These include the kinetic curves of compositions 2 and 4, which are characterized by periods of active water separation, followed by stages of process stabilization ("plateaus"). The second type ("plate-forming"), observed for compositions 3 and 5, is described by a sharp initial separation of water followed by reaching a constant level. The third type ("continuous"), demonstrated by composition 1, is characterized by a monotonous and constant increase in the volume of separated water throughout the experiment.

6. Conclusion

As a result of the research, new demulsifiers were synthesized — Composition 1 and Composition 5, which demonstrated superiority over the reference reagent in terms of a set of key indicators (volume of separated water, residual water content in commercial oil and thickness of the intermediate layer). Two methods have been developed and tested as part of the work: A method of multifactorial experimental planning aimed at optimizing the recipe creation process. Methodology for classifying the destruction of a water-oil emulsion.

It has been established that the use of the multifactorial experiment technique can significantly reduce the time spent on developing the target product, minimize the number of unsuccessful tests, and form a rational formulation design based on statistical analysis. This approach provides compositions with an optimal value of the hydrophilic-lipophilic balance for a specific type of petroleum feedstock. Based on the method of destruction of a water-oil emulsion, a classification of the demulsification process into three types is proposed: The stepwise type observed for Compositions 2 and 4, in which periods of active water separation alternate with stabilization stages. A platelike type, characteristic of Compositions 3 and 5, characterized by rapid initial separation of water, followed by the process reaching a constant level. The continuous type identified for Composition 1, in which a monotonous increase in the volume of separated water occurs throughout the experiment.

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