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OBTAINING AND USE OF NONIONIC DEMULSIFIERS IN OIL TREATMENT

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ABSTRACT

The state of the art technology in the field of synthesis and synthesis and research has set properties and structures. The physicochemical properties and the effect of demulsifier concentration on the process of oil demulsification were studied. The results of studies on the synthesis of demulsifiers, based on some local raw materials and their application in the process of demulsification, are summarized. To characterize water-oil dispersions, their qualitative and quantitative indicators are presented. A number of nonionic demulsifiers to dehydrate and desalt water-oil dispersions is given. Results of effective demulsifiers obtained from local and secondary resources of raw materials are provided.

Keywords: oil, demulsifiers, synthesis, gas condensate, dehydration and desalting, glycerin, oleic acid; SAS; DEA; HMTA; oligomerization.

INTRODUCTION

Oils with a high content of saline (10-15 g / l) water entering the primary treatment tanks and AVT units disrupt their technological mode of operation, the process becomes more complicated, the pressure in the desalination and dewatering apparatus increases and productivity decreases, additional heat is expended, etc. In the pre-treatment of crude oils, the process of their demulsification is used [1, p. . 216].

However, due to the lack of production of local analogues in the country, this large-scale process in the fields is still carried out using imported demulsifiers. Taking into account the above, this article discusses the results of experiments on the production of nonionic demulsifiers from existing semi-finished products of chemical enterprises in our country.

Demulsifiers are widely used to prevent formation, as well as to destroy already formed oil emulsions - surfactants (surfactants) that, unlike natural emulsifiers, help to significantly reduce the stability of oil emulsions. The effect of the demulsifier on the oil emulsion is based on the displacement and substitution of less active surfactant natural emulsifiers by the demulsifier adsorbed at the oil-water interface [7].

Natural emulsifiers are natural surfactants in petroleum (asphaltenes, naphthenes, resins, paraffins) and formation waters. Demulsifiers should be more active than emulsifiers. The film formed by the demulsifier is less durable. When the demulsifier accumulates on the surface of water droplets, mutual gravitational forces appear between the latter. As a result, finely dispersed water droplets form large droplets (cracks), which usually remain films around the water globules [3]. The formation of large particles from finely dispersed water droplets under the action of a demulsifier is called flocculation. During flocculation, the surface film of the water globules is sufficiently weakened that it is destroyed and the water globules coalesce. The process of joining water droplets is called coalescence.Good demulsifiers should not only ensure that the dispersed water droplets coalesce in the emulsion, but also destroy the films surrounding them and help to coalesce.

Demulsifiers wrap the particles of mechanical mixtures in a thin film well moistened with water, and such particles are separated from the oil and removed along with the water. Thus, reagents used as demulsifiers for the destruction of petroleum emulsions must have the following properties:

Ability to access oil and water interface;

Leads to flocculation and fusion of water globules;

Moistens the surface of mechanical compounds well [9].

Such universal properties have a limited number of demulsifiers. Many reagents with known necessary properties have been proposed for the treatment of Oil Emulsions for Disposal.

Demulsifiers are usually divided into two groups:

ionic (ion-forming in aqueous solutions) and non-ionic (non-ion-forming in aqueous solutions). Ions, in turn, can be divided into anions and cations, depending on what surfactant groups they contain - anions or cations.

Selective demulsifiers, ie non-ionic surfactants (surfactants) can be used for desalination and dehydration of water-gas-oil-condensate dispersion [2, p. 119] because they dissolve well in both water and oils. Nonionic surfactants with demulsifying properties are obtained by oligomerization of glycerin, followed by esterification of its oligomer with oleic acid. Oligomerization of glycerin with trioxymethylene (paraform or hexamethylenetetramine-HMTA) is a polycondensation reaction lasting 30 minutes at 250 ° C in an acidic environment. Control of the course of the esterification reaction is carried out by volumetric homogenization of the reaction mixture without the rest of the reacting components [5, p. 46-50]. The technology of obtaining a demulsifier based on glycerin, carboxylic acid and hexamethylenetetramine (HMTA) can be mastered in the country, as these semi-finished products are produced in the enterprises of the republic (HMTA - PO). "Navoiyazot", carboxylic acids - at the Kokand oil extraction plant, glycerin - a product of acid hydrolysis of cottonseed oil). Ethanolamines used in the absorption-desorption process of gas purification form their tri-, tetra- and pentamers [3, p. 143].

Pentamers of absorbent (ethanolamines) - tri-, tetra- and diethanolamine (DEA) - were obtained and water was evaporated, followed by vacuum distillation. After purification of the corresponding DEA derivatives, their physicochemical, colloidal and surfactant properties were determined (Table 1).

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Table 1. Composition and properties of spent DEA

name production DEA	Contents DEA in otrab. absorbent,%	Mol. mass, g/mol	d^{20}_{4}, kg/m³	Colloidal Properties			Destruction time. emulsions, min.	Degree of dehydration. oil samples. dispersion
				Solv. in water, %	Viscosity, SPz	persi., %□20 (5 %) dyn/sm²		
1	2	3	4	5	6	7	8	9
DEA	61,2	105,2	1088	□	5,6	67,5	480	72,6
1	2	3	4	5	6	7	8	9
Dimer DEA	15,5	192,0	1124	□	5,7	64,2	270	85,4
Trimer DEA	7,6	280,0	1165	92,0	6,3	62,7	250	89,9
Tetramer	4,8	367,0	1282	90,5	7,4	63,7	210	94,5
Pentamer	3,7	453,6	1330	85,0	□	59,2	240	95,0
Other resin residue	7,2	520,0	1380	56,5	□	61,8	250	94,0

These DEA derivatives may to some extent serve as demulsifiers in the oil desalination process due to their ability to form complexes with petroleum salts [4, p. 222]. The high effect of demulsification of fat dispersions with their help is achieved after their hydrophobization with octyl alcohol or oleic acid, which is based on the reaction of their esterification with spent ethanolamine derivatives (Table 2).

Table 2. Noionic demulsifiers based on DEA derivatives

Name nonionic demulsifier	Color and appearance	Mol. weight, demulsifier	Destiny. weight, kg/m3	Solubility, %		Demulsifying ability, %
				water	Org. solution	
DEA trimer octyl ether	Red, viscous liquid	504,4	1285	100	52,5	95,2
Trioctyl ether DEA tetramer	Red, viscous liquid	708,7	1364	100	46,4	97,0
Trioctyls. ether DEA tetramer	Brown, viscous liquid	786,6	1385	90	52,0	91,5

From the data in Table 2, it is clear that the obtained demulsifiers are well soluble in water (90-100%), 20-50% - in oil and exhibit surfactant properties, the surface tension of water in 0.5% solution is 54.5 -43.8 erg / cm2. Due to these demulsifiers, oil with a moisture content of up to 100 g / t up to 3% is dehydrated and desalinated to 85-90%. All of the above nonionic demulsifiers meet the requirements for their use in the oil preparation process during dehydration and desalination.

Under the conditions of production, Muborakneftegaz STP has organized experimental industrial production of nonionic demulsifiers on the basis of local semi-finished products and chemical wastes. To obtain a demulsifier from water-soluble oligomers of polyhydric alcohols, they were esterified with oleic acid [10].

The synthesis of demulsifiers was carried out at different molar ratios of the interacting components, reaction duration, and temperature conditions. Thus, a glycerin, HMTA, and oleic acid-based demulsifier is conventionally referred to as "KD" - a carboxyl demulsifier based on a condensation reaction with carboxylic acid and HMTA decomposition products of glycerin - CH2O and NH3.

Optimal demulsifying properties have glycerol with HMTA (obtained in a 5: 1 molar ratio) oleic acid 5: 1, reaction temperature 180-185 ^{0}C and CD obtained in the molar ratio. The process takes 5 hours. In terms of demulsification effect at 150 g / t oil flow, KD has very close or even known advantages over Dissolvan 4411 in dehydration and desalination of oils from Dzharkurgan and Kokdumalak fields. At a temperature of 60 ^{0}C and a flow of 150 g / t oil, the volume of water released in 2 hours is 95% of the original oil, 90% and 65% in Dissolvan 4411. without demulsifiers. In this case, 92% of the salts in the original composition are released. The demulsification of Kokdumalak oil is 97% for dehydration and 94% for desalination. KD demulsifier is a nonionic surfactant whose 1% solution at room temperature reduces the surface tension of water to 38 mN / m. The test results of the demulsifier are given in Table 3.

Table 3. Demulsifier test results

Mass ratios of reagents	Reaction temperature (° C)	**Reaction time (hours)**	Residual water content in the tested oil, (%)
Glycerin: HMTA: H2SO4: Oleic acid 10:1:1:1	180- 190	4,5	1,3
Glycerin: HMTA: H2SO4: Oleic acid 10:1:1:1	230- 250	4	0,6
Glycerin: HMTA: Oleic acid 10:1:1	120-140	5	1,7

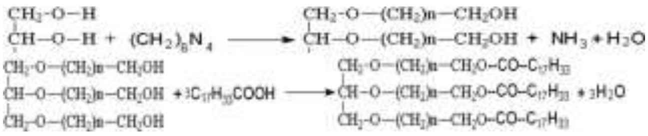
Condensation reactions of glycerin with hexamethylenetetramine (HMTA) and oleic acid have been studied to obtain demulsifiers. The synthesis of the demulsifier was carried out in a 4-neck flask with a capacity of 250 ml, placed in a thermostat (oil bath) equipped with a stirrer, thermometers, reflow condenser and isolating funnel. The course of the reaction was controlled by the degree of decomposition of the HMTA and, accordingly, the amount of formaldehyde released by the condensation reaction with glycerin.

In determining the amount of reactive formaldehyde, the amount of its unreacted residue is taken into account. The degree of thermal decomposition of HMTA is controlled by the amount of ammonia released as a result of the reaction. The second is a two-stage, in the first stage the reaction between glycerin and HMTA, in which esters containing polyalkylene groups are formed, in the second - the reaction between the product formed in the first stage and oleic acid, in which dehydration and esters are formed during desalination, indicating the properties of demulsifying oils.

It is known that GMTA (urotropin) forms ammonia and formic aldehyde:

$$(CH_2)_6N_4 \longrightarrow 6CH_2O + 4NH_3$$

The latter reacts with glycerin to form a compound containing polyoxyalkylene groups:



This product reacts with oleic acid to form an ester with demulsifying properties.

Reaction kinetics under optimal synthesis conditions were studied. However, the molar fractions of glycerin to GMTA are 1: 1.4: 1.5: 1, temperature 100- 120 ^{0}C, 120-140 ^{0}C, 140-180 ^{0}C. Thus, using semi-finished products of domestic production, it is possible to solve the problem of import substitution for local oils demulsifiers. dehydration and desalination of them by destroying stable water-oil emulsions in their composition. In terms of efficiency, the import-substituting demulsifier KD is no less than the imported Dissolvan-4411 reagent.

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