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***Petro Topilnytskyy*[1], *Viktoria Romanchuk*[1], *Sergiy Boichenko*[2] *and Yuri Golych*[3]**

PHYSICO-CHEMICAL PROPERTIES AND EFFICIENCY OF DEMULSIFIERS BASED ON BLOCK COPOLYMERS OF ETHYLENE AND PROPYLENE OXIDES

[1]*Lviv Polytechnic National University, 12, S.Bandery str., 79013 Lviv, Ukraine*
[2]*National Aviation University, 1, Komarova Ave., 03680 Kyiv, Ukraine*
[3]*JSC "Ukrtatnafta", 3, Svishtovska str., Poltavska region, Kremenchuk, Ukraine*

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Abstract. The investigation results about physico-chemical properties of block copolymers based on ethylene and propylene oxides and their solutions which may be used as demulsifiers for oil emulsions have been represented. The dependence of their physico-chemical properties on the content of oxyethylene and oxypropylene groups in the molecule has been determined. On the basis of the technological suitability a series of block copolymers was chosen and their demulsified ability was examined. The increase of ethylene oxide content in the macromolecule positively affects the blockcoplymer demulsified ability.

Keywords: emulsion, demulsifier, dehydration, desalting, degree of dehydration.

1. Introduction

Water and dissolved inorganic salts accompany crude oil in the layer. During oil extraction the brine water pressure pushes oil from porous rocks to the wells. Depending on the layer properties, the velocity of oil extraction, its viscosity and other factors the water content in the oil may vary from 1 to10 % at the initial stage of well exploitation (formation of water in oil emulsion type) to 80–90 % if the well has been operated for a long time (formation of oil in a water emulsion type). The content of water, salts and impurities in the oil affects its processing, namely technological regime of the atmospheric-and-vacuum distillation unit, increases the pressure in the apparatus, reduces productivity and increases the transportation cost.

Under modern pretreatment conditions the crude oil is dehydrated and desalted by combining different methods of emulsions destruction: mechanical (filtration, centrifugation, sonication), thermal (heating and settling under atmospheric pressure), electric (treatment in AC/DC electric field) and chemical ones (addition of demulsifiers) [1-7]. For the crude oil desalting the following combined method is widely used at the refinery: the oil is thermochemically settled with demulsifiers under overpressure and then the emulsion is treated in high voltage electric field [3-5]. Large amount of salts is extracted together with water during dehydration. The residual water content after dehydration is about 0.1 %, and the residual amount of salt is up to 5 mg/l [8].

The right choice of demulsifiers determines the efficiency of dehydration and desalting. The demulsifier promotes the water drops dispersion while it is absorbed on their interfacial surface. Displacing natural emulsifying agents from the drops surface the demulsifier forms the hydrophilic adsorption layer without structural and mechanical strength. In such a way the drops join each other and form the larger ones. In order to destruct the emulsion the demulsifier should have good wetting properties to transfer emulsifying particles inside the volume. The demulsifiers contribute to a clear separation of the phases, exclude the possibility of intermediate emulsions formation and thus lighten the operation of electrical desalting plants.

The surfactants in aqueous solutions are used as demulsifiers. They are divided into three main groups: anion-active, cation-active and non-ionogenic ones. Anion-active and cation-active substances in aqueous solutions dissociate into ions, while non-ionogenic substances do not form ions. The demulsifiers of non-ionogenic type are the most effective ones [9]. When using non-ionogenic demulsifier in the electric field their efficiency increases by several times.

Today around 200–250 demulsifiers are widely known in the world. They are produced by ICI, Exxon, Bayer, SDOilB.V. and Clariant firms. But despite the large number of studies the development of effective demulsifiers remains the key problem. It is connected with the increase of water content in oil, the preparation of different oils emulsions, as well as changes in oil physico-chemical properties and properties of brine water.

The first national non-ionogenic demulsifier was OP-10 – oxyethylated mono- and dialkylphenols. Compared to anion-active demulsifier NChK that was used in almost all refineries of the former Soviet Union, OP-10 was more effective: its average consumption was 40–50 g/t of oil during desalting. As a result, a series of non-ionogenic demulsifiers was synthesized on the basis of alkylphenols, which differed by the origin of raw materials. For example, demulsifier VNII NP-58 was developed on the basis of by-products from ionol-additive production; KAUFE14 – on the basis of phenols extracted from coal tar; UFE – on the basis of high-boiling coal phenols, *etc*. [9]. Despite the fact that the demulsifiers based on alkylphenols were less effective they showed the high selectivity in the destruction of different types emulsions compared to other oxyethylated products.

The demulsifiers produced *via* oxyethylation of fatty acids > C_{20} were found to be more effective. The first demulsifier was called OZhK. In addition to it, a number of other demulsifiers (KS-59, OMZhK, ChNPZ-59, DSTOE) was produced. However, their efficiency and production technology were worse compared to those of OZhK, the consumption of which was 20–40 g/t at the desalting plants and 50–70 g/t – at the oil-fields.

The block copolymers of ethylene and propylene oxides, derived from propylene-, ethylene glycols, ethylenediamide and monoethanolamine, have the highest demulsifying activity among non-ionogenic surfactants. The high efficiency of compounds of such a type is stipulated by the polypropylene glycol as the hydrophobic surfactant part. Its molecular weight may be changed within a wide range. By varying the ratio of polyoxypropylene glycol and polyoxuethylene glycol molecular weights in block copolymers macromolecules we may obtain a wide range of compounds with different properties [7, 8].

The aim of the present work is to determine the physico-chemical properties of demulsifiers based on block copolymers of ethylene and propylene oxides, as well as their effectiveness depending on the molecular weight and the ratio of ethylene and propylene oxides in the active molecule by the following parameters:

- specific consumption of the demulsifier;
- settling time of the emulsion;
- content of water remained in oil after the dehydration process;
- settling temperature of oil emulsion.

2. Experimental

2.1. Surface Tension

The block copolymers based on ethylene and propylene oxides were produced by JSC Barva and chosen in such a way that they may be further used in the oil-refining industry for oil dehydration and desalting. The investigated non-ionogenic substances were synthesized *via* adding of propylene oxide to propylene glycol and then ethylene oxide was added to polyoxypropylene glycol. The ratios between average molecular weights of oxypropylene and oxyethylene blocks as well as the average molecular weight of prepared block copolymer determine the demulsifying activity of the demulsifier. The block copolymers were divided into three groups according to their weights (3200, 3500 and 6000). The oxyethylene/oxypropylene (OE/OP) group ratios were different. The characteristics are represented in Table 1.

Table 1

Initial characteristics of block copolymers based on ethylene and propylene oxides

Sample number	Molecular weight	OE/OP ratio, %
1	3200	85/15
2	3200	90/10
3	3200	95/5
4	3500	75/25
5	3500	85/15
6	3500	95/5
7	6000	75/25
8	6000	85/15
9	6000	95/5

The oil emulsion was prepared from Gnidynci oil by the known method [5]. The water content was 3.5 %.

The block copolymer solutions were prepared as follows:

- aqueous solution was prepared by adding 50 % of block copolymer, 10 % of isopropyl alcohol (IPA) and 40 % of ditilled water;
- solution with a solvent was prepared in the same way only 40 % of the solvent was added instead of water.

We obtained 18 solutions of block copolymers for which density, viscosity and the freezing point were determined by the known methods [10, 11].

2.2. Investigation Procedure

To determine the demulsifying ability the sample (200 ml) is loaded into the extractor equipped by a mechanical stirrer and water-jacket. The temperature is sustained by a thermostat.

The samples are sustained at 333 K for 15 min. Then the demulsifier (as 10% aqueous solution) is added by a micropipette and the samples are stirred for 5 min. After this the emulsion is settled for 1, 2 and 3 h. The amounts of demulsifiers are 10, 50, 70 and 100 g/t. The water is separated and its volume is measured. To control the balance the residual content of water in the emulsion is determined.

The degree of dehydration (%) was calculated in accordance with the formula (1):

$$Z = \frac{V_1 - V_2}{V_1} 100\% \qquad (1)$$

where V_1 – water volume in the initial emulsion, ml; V_2 – water volume in the emulsion after dehydration, ml.

For every sample three parallel experiments were carried out and the arithmetical mean value was taken. If the error is more than 5 %, the experiments were repeated. The results are given in Tables 2-6 and Figs. 1-7.

3. Results and Discussion

The experimental results, namely the freezing point, viscosity and density of different block copolymers are represented in Table 2.

The increase of the ethylene oxide content in the sample increases the freezing point. The same situation is observed for the samples with the same molecular weight. The increase of OE in the molecule by 5 % increases the freezing point by 8–10 K. With the increase of the molecular weight the freezing point increases by 2.6–10.5 K at constant OE/OP ratio.

The viscosity is determined at 323 K. It proportionally depends on the molecular weight. For the samples 1–3 the increase in viscosity is observed by 7–11 cSt with the increase of OE content by 5 % in the molecule with *M* = 3200. The change of viscosity is more dynamic (by 7–22 cSt) in the molecules with greater molecular weight (*M* = 3500) while OE content increases from 75 to 95 %. The highest value of viscosity (220–291 cSt) was found for the molecule with *M* = 6000. Here we also observe the greatest difference between the viscosities (71 cSt) for the samples with OE content of 75 and 95 %.

The density of block copolymers with *M* = 3200 is 1021–1031 kg/m^3 and also depends on oxyethylene groups content in the molecule. The increase in OE content increases the density. If we compare the samples with different molecular weight we observe the increase in density with the increase of their molecular weight.

For the solutions of block copolymers with water and solvent we determined density, viscosity and solutions behavior at low temperatures. The results are represented in Tables 3 and 4.

The density and viscosity of block copolymers aqueous solutions decrease compared with those of pure bases. The density and viscosity of block copolymers with *M* = 6000 increases more sharply with the increase in OE content from 75 to 95 % compared with the same values of block copolymers with *M* = 3200 (Tables 2 and 3).

Table 2

Physico-chemical properties of the block copolymers pure bases

Sample number	Molecular weight	OE/OP ratio, %	Freezing point, K	Viscosity at 323 K, cSt	Density at 323 K, kg/m^3
1	3200	85/15	280.5	175.0	1021
2	3200	90/10	289.0	182.0	1028
3	3200	95/5	297.5	193.2	1031
4	3500	75/25	283.1	182.0	1012
5	3500	85/15	290.8	191.0	1030
6	3500	95/5	301.1	215.0	1036
7	6000	75/25	289.1	220.0	1041
8	6000	85/15	297.7	245.0	1049
9	6000	95/5	311.2	291.0	1051

Table 3

Investigations of block copolymers aqueous solutions (50 % of block copolymer, 40 % of water, 10% of IPA)

Sample number	Molecular weight	OE/OP ratio, %	Viscosity at 293 K, cSt	Density at 293 K, kg/m^3	Frozen at 263 K
1	3200	85/15	989.0	71.2	non-frozen
2	3200	90/10	992.5	73.9	non-frozen
3	3200	95/5	994.0	78.2	non-frozen
4	3500	75/25	990.0	74.7	non-frozen
5	3500	85/15	993.5	80.2	non-frozen
6	3500	95/5	996.5	91.3	non-frozen
7	6000	75/25	999.0	102.6	non-frozen
8	6000	85/15	1003.0	120.8	non-frozen
9	6000	95/5	1004.0	135.7	frozen

Table 4

Investigations of block copolymers solutions in the solvent (50 % of block copolymer, 40 % of solvent, 10% of IPA)

Sample number	Molecular weight	OE/OP ratio, %	Viscosity at 293 K, cSt	Density at 293 K, kg/m^3	Frozen at 263 K
1	3200	85/15	933.0	11.9	non-frozen
2	3200	90/10	936.5	12.6	non-frozen
3	3200	95/5	938.0	13.9	non-frozen
4	3500	75/25	934.0	13.5	non-frozen
5	3500	85/15	937.5	14.3	non-frozen
6	3500	95/5	940.5	15.2	non-frozen
7	6000	75/25	943.0	16.1	non-frozen
8	6000	85/15	947.0	17.9	non-frozen
9	6000	95/5	948.0	19.3	frozen

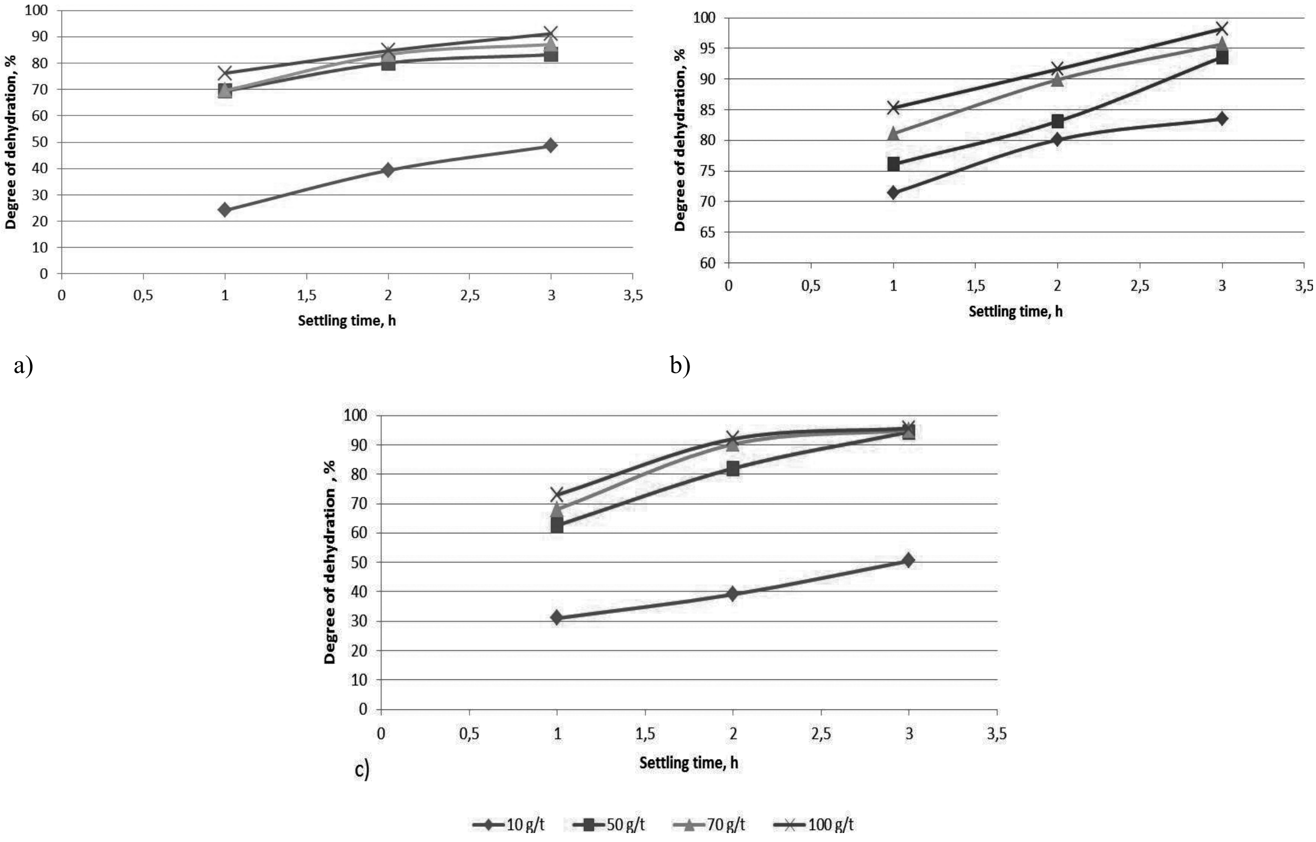
Table 5

Demulsifying ability of block copolymers

Demulsifier consumption, g/t	Degree of dehydration, %, during settling for		
	60 min	120 min	180 min
1	2	3	4
Sample 1. *M* =3200; OE/OP = 85/15			
10	24.1	39.3	48.5
50	68.1	80.1	83.2
70	69.6	83.3	87.1
100	76.2	84.7	91.2
Sample 2. *M* = 3200; OE/OP = 90/10			
10	71.4	80.1	83.5
50	76.1	83.1	93.6
70	81.1	89.9	95.7
100	85.3	91.6	98.2
Sample 3. *M* = 3200; OE/OP = 95/5			
10	31.0	39.1	50.5
50	62.6	82.0	85.0
70	68.1	90.2	95.0
100	73.0	92.0	95.6
Sample 4. *M* = 3500; OE/OP = 75/25			
10	39.9	54.0	61.2
50	64.1	67.0	68.5
70	72.2	75.7	77.1

Table 5 (Continued)

1	2	3	4
100	78.6	80.8	82.3
Sample 5. *M* = 3500; OE/OP = 85/15			
10	46.6	59.0	59.0
50	61.7	64.7	75.0
70	83.2	89.7	90.8
100	97.6	98.2	98.2
Sample 6. *M* = 3500; OE/OP = 95/5			
10	17.9	43.4	57.4
50	79.2	80.7	81.4
70	86.5	90.8	92.1
100	91.5	92.9	95.1
Sample 7. *M* = 6000; OE/OP = 75/25			
10	24.4	32.2	42.8
50	31.2	47.6	63.1
70	35.5	57.8	67.9
100	68.0	80.0	85.9
Sample 8. *M* = 6000; OE/OP = 85/15			
10	23.5	57.9	75.1
50	53.5	67.8	79.6
70	70.5	77.0	82.2
100	80.5	88.0	92.2



a)

b)

c)

Fig. 1. The dependence of emulsion dehydration degree on the settling time and demulsifies ($M = 3200$) consumption at different ratios OE/OP: 85/15 (a); 90/10 (b) and 95/05 (c)

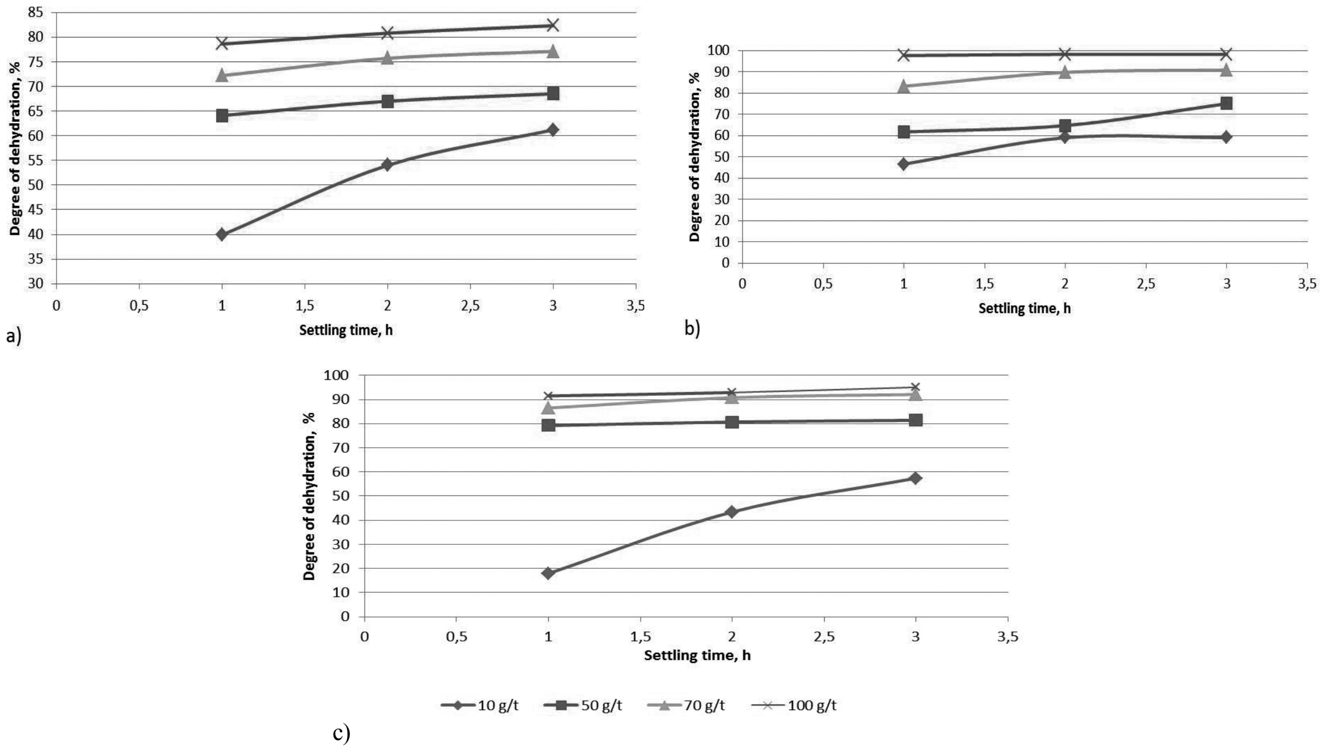


Fig. 2. The dependence of emulsion dehydration degree on the settling time and demulsifies ($M = 3500$) consumption at different ratios OE/OP: 75/25 (a); 85/15 (b) and 95/5 (c)

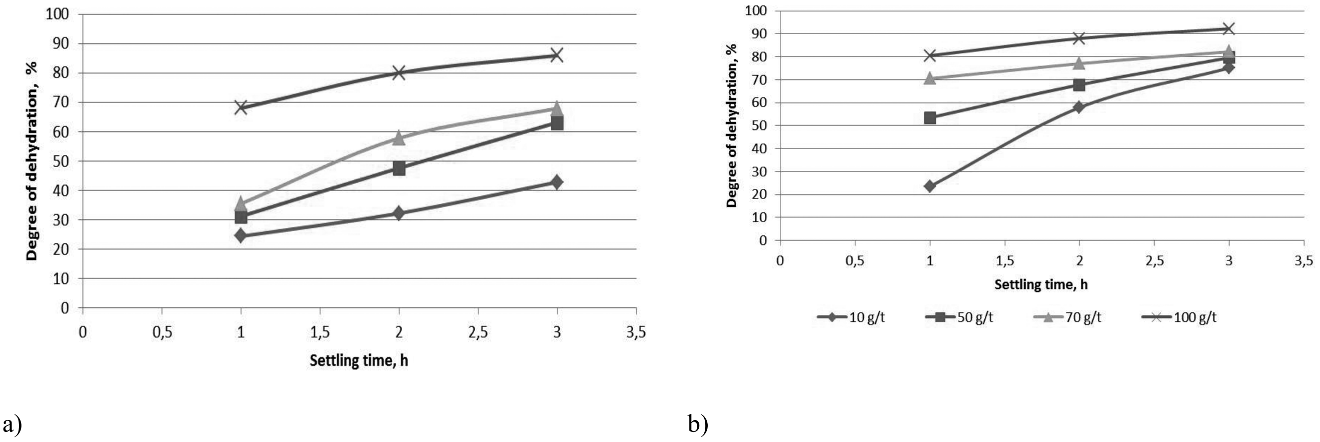


Fig. 3. The dependence of emulsion dehydration degree on the settling time and demulsifies ($M = 6000$) consumption at different ratios OE/OP: 75/25 (a) and 85/15 (b)

While investigating the aggregate state of block copolymers at low temperatures it was determined that aqueous and solvent solutions were not frozen at the temperatures above 263 K. The only one exclusion was the solution of the demulsifier with M = 6000 and ethylene oxide content of 95 %. It was frozen at 263 K and it would be the negative factor while feeding the demulsifier to the plant in winter.

Thus, in all cases the increase of OE/OP ratio and molecular weight increases density, viscosity and the freezing point of the samples.

For further investigations, in particular the investigations of the demulsifying ability, we chose samples 1–8. The sample 9 is frozen at 263 K in both water and solvent; hence it is unusable due to above-mentioned reasons.

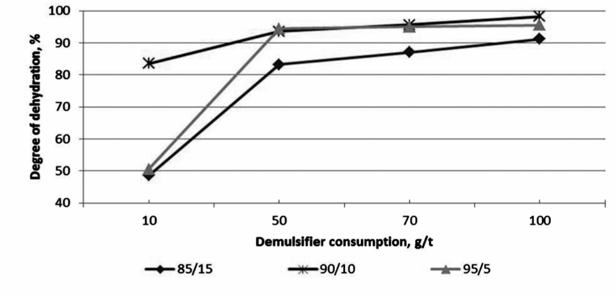


Fig. 4. Dependence of emulsion dehydration degree on the demulsifier ($M = 3200$) consumption at different ratios OE/OP and settling time of 3 h

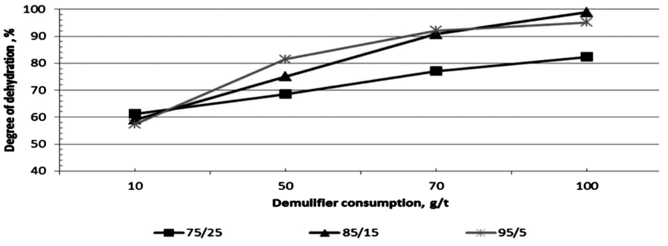


Fig. 5. The dependence of emulsion dehydration degree on the demulsifier ($M = 3500$) consumption at different ratios OE/OP and settling time of 3 h

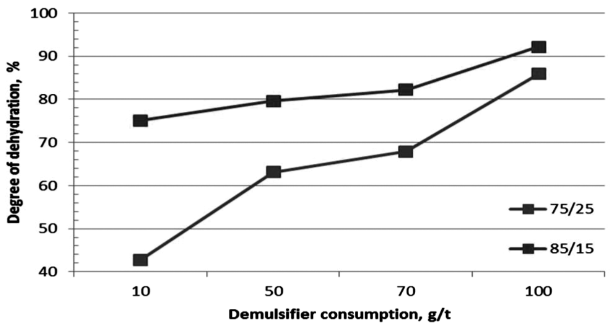


Fig. 6. The dependence of emulsion dehydration degree on the demulsifier ($M = 6000$) consumption at different ratios OE/OP and settling time of 3 h

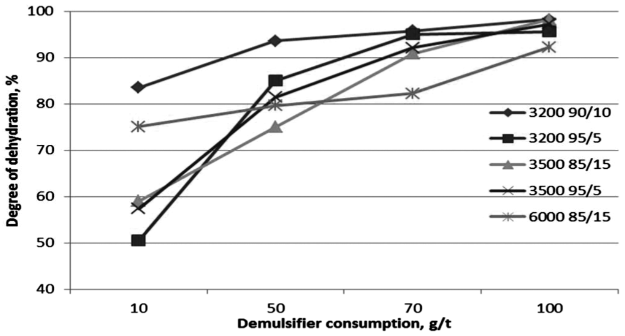


Fig. 7. The dependence of dehydration degree of different block-copolymers at different consumptions

Table 6

Degree of block copolymers dehydration for the settling time of 3 h

Sample number	Molecular weight	OE/OP ratio	Demulsifier consumption, g/t	Degree of dehydration, %
2	3200	90/10	10	83.5
			50	93.6
			70	95.7
			100	98.2
3	3200	95/5	10	50.5
			50	94.4
			70	95.0
			100	95.6
5	3500	85/15	10	59.0
			50	75.0
			70	90.8
			100	98.2
6	3500	95/5	10	57.4
			50	81.4
			70	92.1
			100	97.2
8	6000	85/15	10	75.1
			50	79.6
			70	82.2
			100	92.2

The investigation results are given in Table 5 and Figs. 1-7. The degree of dehydration was calculated according to the formula (1).

Thus, the greatest demulsifying ability is observed after 3 h of emulsion settling. Taking this fact into account we compared the dehydration degree of block copolymers with M = 3200, 3500 and 6000 (Figs. 4, 5 and 6, respectively) at different OE/OP ratios and different values of consumption.

The investigations of demulsifying ability dependence on demulsifiers consumption were carried out. At the values of consumption 10–50 g/t the degree of dehydration is insufficient for all samples. It is ineffective from the technological point of view. The comparison of demulsifying ability at the consumption of 70 g/t shows the lowest demulsifying ability for the block copolymer with M = 6000. Other block copolymers show the efficiency at the level of 90 %. The increase of block copolymer consumption to 100 g/t increases the degree of dehydration by another 5 %. It achieves 97–98 % for the block copolymers with M = 3200 and 3500.

On the basis of above-mentioned results we selected the block copolymers with the greatest demulsifying ability. Table 6 and Fig. 7 represent the comparative data for the block copolymers with different molecular weight and different values of consumption at the settling time of 3 h.

4. Conclusions

The experiments show that density, viscosity and freezing point of block copolymers increase with the increase of their molecular weight and OE content in macromolecules.

The block copolymers with the molecular weight of 3200 and 3500 have the great demulsifying ability (97–98 %) at the demulsifier consumption of 100 g/t. The highest value of demulsifying ability is observed for both copolymers with OE/OP ratio of 90/10 and 85/15, respectively.

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ДОСЛІДЖЕННЯ ФІЗИКО-ХІМІЧНИХ ВЛАСТИВОСТЕЙ ТА ЕФЕКТИВНОСТІ ДЕЕМУЛЬГАТОРІВ НА ОСНОВІ БЛОК-КОПОЛІМЕРІВ ОКСИДІВ ЕТИЛЕНУ ТА ПРОПІЛЕНУ

Анотація. *Наведено результати досліджень фізико-хімічних властивостей блок-кополімерів на основі оксидів етилену та пропілену та їх розчинів, які можуть бути використані як деемульгатори нафтових емульсій. Встановлено залежність фізико-хімічних властивостей блок-кополімерів та їх розчинів від вмісту оксиетиленових та оксипропіленових груп в молекулі. На основі технологічної придатності відібрані блок-кополімери та їх розчини для досліджень їх деемульгуючої здатності. Встановлено, що збільшення вмісту оксиду етилену в макромолекулі позитивно впливає на деемульгуючу здатність блок-кополімерів. На основі одержаних результатів відібрані речовини для досліджень у різних вуглеводневих середовищах.*

Ключові слова: *емульсія, деемульгатор, зневоднення, знесолення, ступінь зневоднення.*