The stability of emulsions in the presence of additives

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The influence of different additives on the effective *HLB* values of non-ionic emulsifiers was studied by the method of the determination of the phenol index values and by the determination of the emulsion inversion point in the system with xylene as the oil phase. Ethanol, glycerol and ethylene glycol were investigated as additives. The method of the determination of the phenol index value was applied on two homologous series of non-ionic emulsifiers: nonylphenolpolyglycolethers with 10, 15, 23 and 30 moles of bound ethylene oxide and polyglycolethers of fatty alcohols (C_{16}–C_{18}) with 15, 20 and 23 moles of bound ethylene oxide. The additives were applied in the concentration of 5, 10, 15 and 20 %. The results showed that ethanol and ethylene glycol increased the phenol index value. The influence of ethanol was more pronounced. On the contrary, glycerol reduces the phenol index value. There were small differences in the influence of these additives on certain members of both homologous series, but the general trend is presented here. The influence of the same additives on the values of the emulsion inversion point was investigated in the system with xylene and nonylphenolpolyglycolethers with 10 moles of bound ethylene oxide. Ethanol and ethylene glycol were applied in the concentrations of 1, 5, 10 and 15 %, and glycerol in 5,7.5,10 and 15 %. The results showed that ethanol and ethylene glycol reduce the emulsion inversion points, while glycerol increases them. On the basis of these investigations it can be concluded that ethanol and ethylene glycol could contribute to an increase in the stability of emulsions, glycerol has the opposite effect. The results of both applied methods are in accordance.

Keywords: additives, emulsion, phenol index value, emulsion inversion point.

INTRODUCTION

It is known that some additives can cause either and increase or a decrease in the effective *HLB* of an emulsifier as indicated by changes in different measurable parameters, depending on the nature of the additives, as well as the concentration and type of non-ionic emulsifier. This means that additives can influence the stability of an emulsion. Thus additives which decrease the effective *HLB* cause a decreased stability of O/W emulsions. On the other hand, additives which increase the effective *HLB* increase the stability.

Marszal[1–5] developed the method of phenol titration for the determination of effective *HLB*. Actually, the effective *HLB* (in the range of 12–15) can be determined by

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measurement of the cloud point. However, the temperature of 110 ºC sets a practical limit for the exact determination of the effective *HLB* using this procedure. Cloud point curve above 110 ºC can generally be assumed to be almost independent of the chain length. If identification of long chain ethoxylates is desired by this method, the determination can be made using a solution of sodium chloride, which, like most electrolytes, depresses the cloud point. However, the presence of a salt in a solution of a surfactant has a significant effect on the *HLB*.[6] Another way of extending the range of the cloud point method is to perform the measurements under a pressure sufficiently high to prevent the boiling of water.

It seems that the above mentioned method developed by Marszall is much easier to use for the determination of the effective *HLB* in the presence of additives when the polyether chain contains more than 15 ethoxy units. The procedure is similar in principle to that used by Karabinos[7] for the determination of the chain length of polyoxyethylene where the hydrophobic group is known. The phenol titration (index) value is based on the titration of aqueous solutions of non-ionic surfactants using phenol.

On the other hand, the method of the determination of the emulsion inversion point (*EIP*) has been used as screening test for the *HLB* for the selection of an emulsifier system.[8–11] This method can also be used for the investigation of the effects of different additives on the *EIP* value of certain emulsifier. It is well known that the emulsion inversion point (*EIP*) is the point at which an emulsion changes from the water-in-oil (W/O) to the oil-in-water (O/W) form, at a constant temperature.

In the present investigations, the effect of various additives on the effective *HLB* values of non-ionic emulsifiers was studied by determining both the phenol index values and the emulsion inversion point.

EXPERIMENTAL

Two homologue series of non-ionic emulsifiers were used: nonylphenolpolyglycolethers with 8–30 moles of bound ethylene oxide and polyglycolethers of fatty alcohols (C_{16}–C_{18}) with 10–23 moles of bound ethylene oxide. Both homologous series were of commercial quality (Hoechst, Frankfurt, Germany) and were used without further purification. Ethanol (Alkaloid, Skoplje, Macedonia), glycerol (Zorka, Šabac, Yugoslavia) ethylene glycol (Kemika, Zagreb, Croatia), xylene (Kemika, Zagreb, Croatia) and phenol (Merck, Darmstadt, Germany) (pure grade) were used.

For the determination of phenol index values, a 5 % aqueous phenol solution was added dropwise to a continuously stirred equimolar (0.025 M) surfactant solution (50 g) at a constant temperature (298 K) until distinct turbidity marked the end point of the titration.[2] The volume of phenol solution which was added represents the phenol index. The same procedure was used for the determination of the phenol index value in the presence of additives. The members from two series of non-ionic: nonylphenolpolyglycolethers with 10, 15, 23 and 30 moles of bound ethylene oxide and polyglycolethers of fatty alcohols (C_{16}–C_{18}) with 15, 20 and 23 moles of bound ethylene oxide were used. Ethanol, glycerol and ethylene glycol (5, 10, 15 and 20 %) were used as additives.

For the determination of the emulsion inversion point (*EIP*), measured volumes (50 cm^3) of the oil phase containing nonylphenolpolyglycolether with 10 moles of bound ethylene oxide (2 %), alone and in the presence of the above mention additives were used.[8] The *EIP* was determined by adding increments (1 cm^3) of water from a burette (5 cm^3). After each addition, the emulsion was mixed for 20 s. After that, the type of the emulsion was determined by means of a conductivity meter (conductometer MA 5966, Iskra, Kranj, Slovenia) at a constant temperature (293 K). All the samples

were measured until the desired reproducibility was obtained. Ethanol and ethylene glycol (1, 5, 10 and 15 %), and glycerol (5, 7.5, 10 and 15 %) were applied. The emulsion inversion point (*EIP*) was calculated as the relation between the volume of water (cm^3) that had to be added to cause inversion and the volume of the oil present (50 cm^3).

The *HLB* values were calculated on the basis of the Griffin formula[12] for the nonylphenolpolyglycolethers and were taken from the producer's declaration for the polyglycolethers of fatty alcohols.

RESULTS AND DISCUSSION

The correlation between the *HLB* values and the phenol index values (*V*) for the nonylphenolpolyglycolethers and polyglycolethers of fatty alcohols are shown in Fig. 1. Linear correlations were found between the phenol index values, defined as the volume (in cubic centimeters) of a 5 % phenol solution required for the titration and the *HLB* of several homologous series of non-ionic surfactants using equimolar concentrations. The higher the *HLB*, the more phenol is required to reach the end point. It is considered that when phenol is progressively added to a solution of a non-ionic surfactant, the turbidity at room temperature (298 K) is not due to the excess of the solubilizate but rather to an actual depression of the cloud point. Thus, the turbidimetric measurement of a solution of a non-ionic surfactant under isothermal conditions as function of the added amount of phenol is related to the cloud point phenomenon. The effect on the
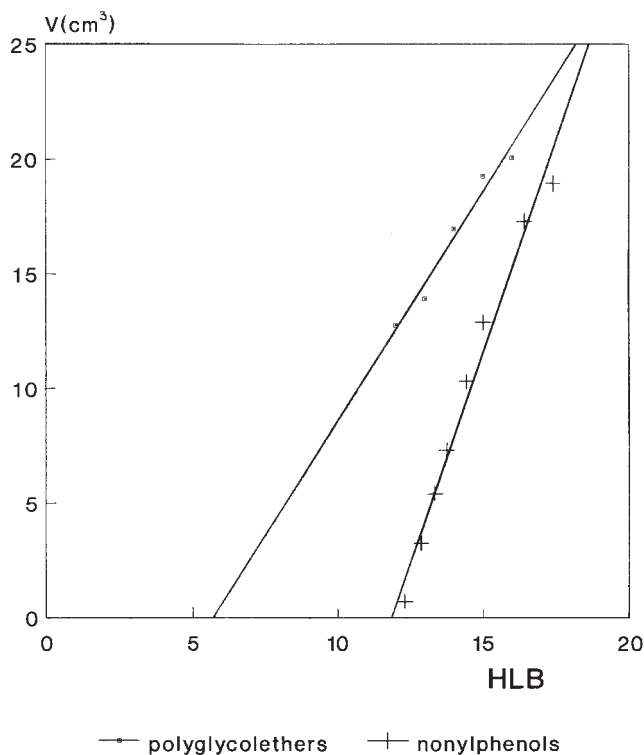

Fig. 1. Phenol index values as a function of *HLB* for nonylphenolpolyglycolethers and polyglycolethers of fatty alcohols.

cloud point of an increase in the phenol concentration resembles closely the effect of the reduction of the number of oxyethylene units in the polyoxyethylene chain in homologous series of non-ionic surfactants containing the same lipophilic group. This suggests that the mechanism involves a reduction in the hydrophilicity of the polyoxyetylene chains due to the binding of phenol. Thus, the addition of phenol to a dilute surfactant solution can have the same effect as increasing the temperature.[13]

In discussing the obtained dependence, it can be seen that the slope for the nonylphenolpolyglycolethers is steeper than that for the polyglycolethers, *i.e.,* the polyglycolethers required more phenol solution to reach the end point than the homolognes of nonylphenols for the same *HLB*.

The influence of the additives (ethanol, ethylene glycol, glycerol) on the phenol index value for nonylphenolpolyglycolether with 10, 15, 23 and 30 moles of bound ethylene oxide are presented in Figs. 2 and 3. It can be concluded that ethanol and ethylene glycol increased the phenol index values while the influence of glycerol was just the reverse. Ethanol increased the phenol index values but the influence on the homologue with 10 moles of bound ethylene oxide was more pronounced in any case. The influence of etrhylene glycol was similar to that of ethanol but less pronounced. Glycerol de-
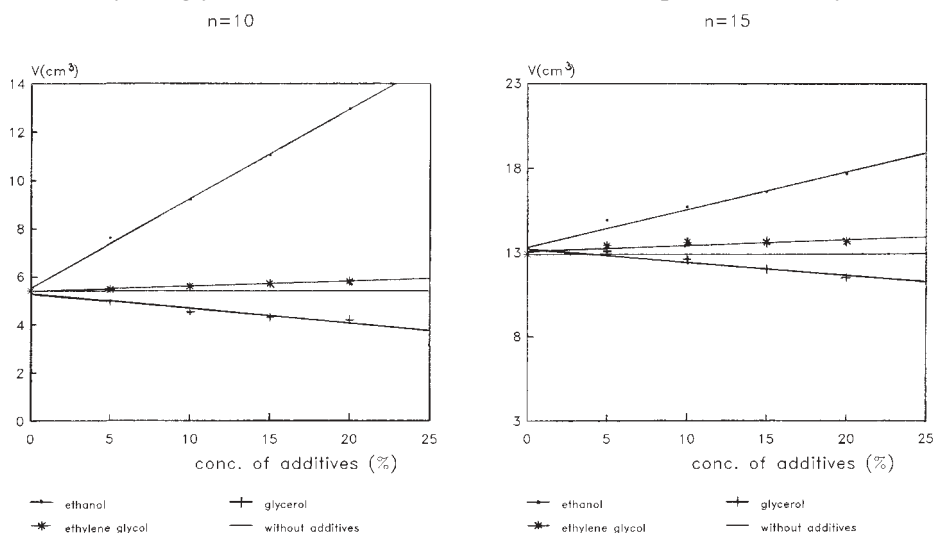

Fig. 2. The effect of additives on the phenol index values for nonylphenolpolyglycolether with 10 and 15 moles of bound ethylene oxide.

creased the phenol index values. The influence of this additive became less, the higher the *HLB* of the emulsifier was. Linear correlations were found in all cases. The obtained results are in accordance with the results of other authors.[1–5,14] The influence of the additives on the polyglycolethers with 15, 20 and 23 moles of bound ethylene oxide are shown in Figs. 4 and 5. As can be seen, ethanol and ethylene glycol caused the phenol index values increase, while glycerol caused them to decrease. Comparing the influence of ethanol and ethylene glycol, it can be said that the former has a stronger effect on the phenol index values.
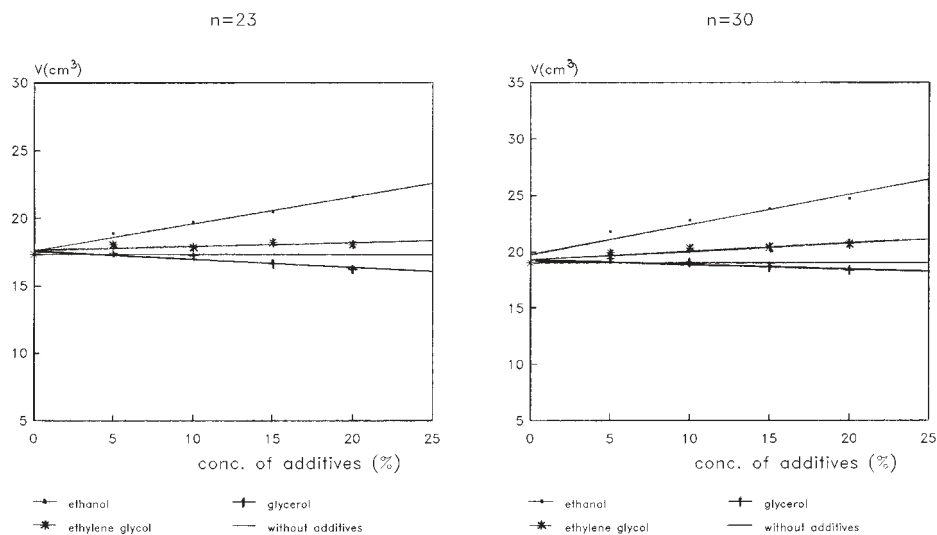
n=23

n=30

Fig. 3. The effect of additives on the phenol index values for nonylphenolpolyglycolether with 23 and 30 moles of bound ethylene oxide.

Additives which change the phenol index values of certain non-ionic emulsifier can change their effective *HLB*. According to this method, the end point appears above a critical micelle concentration.[15] It is known that solute interaction are greater with increasing length of the polyoxyethylene chains. Increasing the hydrophilic chain length increases the aqueous solubility of the monomer and, therefore, decreases the driving forces leading to micellization. The hydrophilic chain can be increased to an extent where no micellization occurs. Such an effect may be achieved when additives are
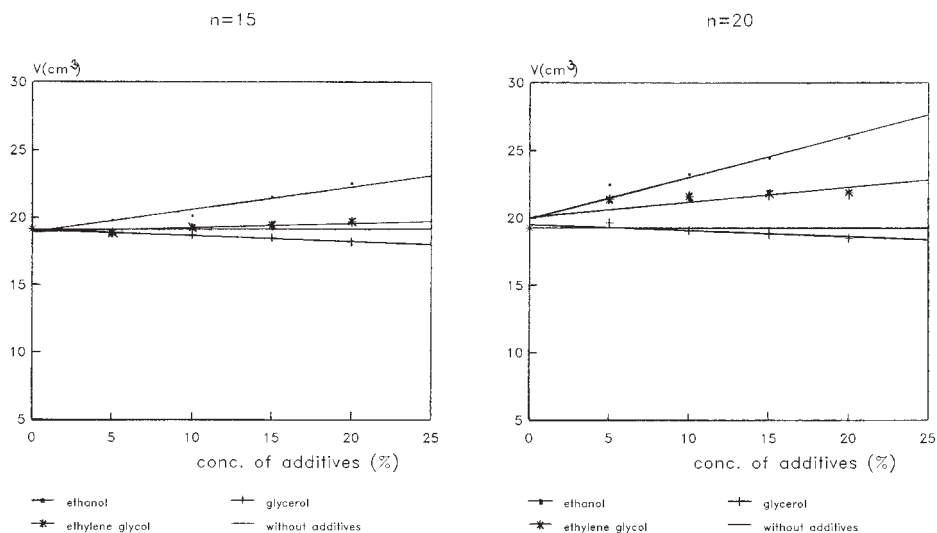
n=15

n=20

Fig. 4. The effect of additives on the phenol index values for polyglycolether of fatty alcohols with 15 and 20 moles of bound ethylene oxide.
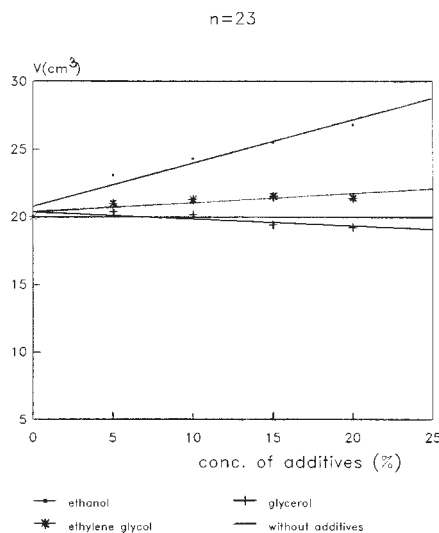
n=23

Fig. 5. The effect of additives on the phenol index value for polyglycolether of fatty alcohols with 23 moles of bound ethylene oxide.

added which tend to make the effective *HLB* of a surfactant higher than its assigned value.[16] Attempts have been made to employ these methods to determine the concentration of an additive which prevents the formation of micelles. Generally, it is very difficult to discuss this topic because there are some solvents in which micelles form independent of concentration and even in the presence of additives. The influence of micelles on emulsification is not completely clear, but it has been found[17–19] that, in some cases, they could cause instability.

Generally, it is known that an emulsion is stable close the critical micelle concentration. The stability of an emulsion decreases as the concentration of emulsifier increases. It could be concluded that micelles cause a decrease of the adsorption of emulsifiers on the interface, which cause instability.

The results obtained using the emulsion inversion point (*EIP*) method in the presence of additives are shown in Fig. 6. For this investigation, the system of nonylphenolpolyglycolether with 10 moles of bound ethylene oxide in xylene as the oil phase was chosen. This choice was made on the basis of earlier investigations with xylene as the oil phase and nonylphenolpolyglycolethers.[11,20] The results showed that ethanol and ethylene glycol reduce the emulsion inversion point, while glycerol increases them. The dependencies between *EIP* and the concentration of additive were not linear. It is considered that additives which tend to change the *EIP* value also change the effective *HLB* value. So, additives which reduced the *EIP* value increase the effective *HLB* value, while additives which have the opposite effect on the *EIP* value reduced the effective *HLB* value.[2] It can be concluded that ethanol and ethylene glycol tend to increase the effective *HLB*, with the influence of the former being stronger. The influence of both additives became stronger as their concentration increased. The influence of glycerol was just the opposite. This additive reduced the effective *HLB* value by an amount depending on the applied concentration.

The influence of additives can be explained by means of cohesive energies.[21] It is well established that specific cohesive energies are involved in emulsions. The magni-
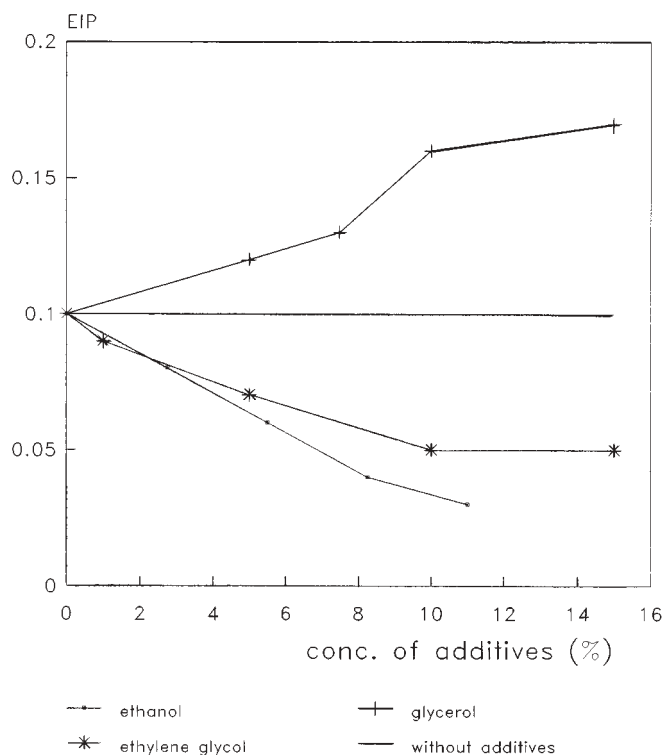
Fig. 6. The effect of additives on the *EIP* value for the nonylphenolpolyglycolether with 10 moles of bound ethylene oxide.

tude and ratio of two cohesive energies, the cohesive energy of a lipophile for the oil (A_{LO}) and of a hydrophile for water (A_{HW}) molecules, determine the structure and stability of an emulsion as defined by the cohesive energy ratio (*CER*). The change of the *EIP* value reflects the degree of the change of the cohesive energy of the same lipophile for oil phase (A_{LO}) in the presence of various additives or, in other words, the degree of molar volume and chemical match of the lipophyle and the oil. This, in turn, changes the cohesive energy ratio (*CER*) of the emulsion. The decrease or increase of the *EIP* value depends on the rate of equilibration of the values of the cohesive energies of the hydrophile for water (A_{HW}) and of the lipophile for oil (A_{LO}) molecules. This introduction of some hydrophilic additives enriches the value of the cohesive energy of the hydrophile on the waterside of the interface, *e.g.,* by the formation of hydrogen bonds with the –O··· of the EO. A decrease of the *EIP* value then follows, since the cohesive energy ratio of the emulsion, *CER* = 1, is attained faster.

The effect of additives on the *HLB* of an emulsifier is reflected on the emulsion stability. On the basis of these investigations, it can be concluded that ethanol and ethylene glycol could contribute to an increase in the stability of an emulsion, while glycerol has the opposite effect. The results of both applied methods are in accordance. Comparing the influence of the additives on both series of non-ionic emulsifiers, it can be concluded that the main influence of the additives occurs to the hydrophilic part of the

molecules as the changes have the same trend, in spite of differences in the hydrophobic part. According to the obtained results, it can be concluded that the influence to the hydrophobic part is negligible. A comparison of these two methods indicates that the *EIP* method affords additional advantages because it takes into account the nature of the oil present and so on the interaction between the emulsifier and the oil.

CONCLUSION

Linear correlations were found between the phenol index values, defined as the volume (in cubic centimeters) of a 5 % phenol solution required for the titration and the *HLB* of both homologous series of examined emulsifiers, using equimolar concentrations. This dependency can be used for calculating effective *HLB* values for the emulsifiers in the presence of additives.

Ethanol and ethylene glycol increase the phenol index values (increase the effective *HLB*) with the influence of the former being more pronounced in every case. Glycerol has just the opposite influence. The dependencies between the concentration of the additives and the phenol index values are linear.

Ethanol and ethylene glycol decrease the values of the emulsion inversion point (*EIP*) (increase the effective *HLB*). Glycerol causes and increase in the values of the *EIP* (decrease of the effective *HLB*). The influence of the additives was more pronounced at higher concentrations. The dependencies between the *EIP* and the concentration of the additives were not linear.

Ethanol and ethylene glycol could contribute to an increase of the stability of an emulsion, while glycerol has the reverse effect.

The results of both applied methods are in accordance.

И З В О Д

СТАБИЛНОСТ ЕМУЛЗИЈА У ПРИСУСТВУ АДИТИВА

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У раду је праћен утицај различитих адитива на ефективне *HLB* вредности нејонских емулгатора, одређивањем фенолних индекса и методом одређивања прелазне тачке у систему са ксилолом као уљном фазом. Као адитиви примењени су етанол, глицерол и етиленгликол. Метод одређивања фенолних индекса примењен је на две хомологе серије нејонских емулгатора и то: нонилфенолполигликолетре са 10, 15, 23 и 30 молова везаног етилен оксида и полигликолетре масних алкохола (C_{16}–C_{18}) са 15, 20 и 23 молова везаног етилен оксида. Адитиви су примењени у концентрацијама 5, 10, 15 и 20 %. Резултати су показали да етанол и етиленгликол утичу на повећање вредности фенолног индекса, при чему је утицај етанола више изражен. Супротно, присуство глицерола доводило је до смањења вредности фенолног индекса. Уочене су мале разлике утицаја ових адитива на поједине чланове испитиваних хомологих серија, али је овде дат генерални тренд. Утицај истих адитива на вредности прелазне тачке био је испитиван у систему са ксилолом као уљном фазом и нонилфенолполигликолетром са

10 молова везаног етилен оксида. Етанол и етиленгликол су били примењени у концентрацијама од 1, 5, 10 и 15 %, а глицерол у концентрацијама 5, 7,5, 10 и 15 %. На основу добијених резултата закључено је да етанол и етиленгликол снижавају вредности прелазне тачке док је утицај глицерола супротан. На основу ових испитивања може да се закључи да етанол и етиленгликол могу да повећају стабилност емулзија, док је утицај глицерола супротан. Резултати обе примењене методе су у сагласности.

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