ВИСОКОМОЛЕКУЛЯРНІ СПОЛУКИ ТА КОМПОЗИЦІЙНІ МАТЕРІАЛИ

UDC 678: 541.64

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AMPHIPHILIC AMINOFUNCIONAL DIESTERETHERS AS DISPERSED SYSTEM STABILIZERS

Statement of a problem. Over the last decades the surfactants have been objects of intensive fundamental and applied studies all over the world. The efficient surface active and emulsifiable properties of these compounds are widely used to control processes of the watering, suspension stabilization, gelling and foaming. These properties provide their practical application in the pharmaceutical, food, wood-pulp, petroleum industry, agriculture and environment purification. In the last years the new area of so-called green chemistry stating task to develop the new compounds including surfactants based on the natural raw materials has been arisen. The usage of substances of natural origin in cosmetics and pharmaceuticals production is popular trend conditioned by the necessity of decreasing of conventional surfactants effects such as toxicity, allergenicity and attaching ability to degrade under natural conditions [1,2].

Review of the latest researches and publications. The review of publications in the area of development of the new surfactants for dispersed systems stabilization showed tendency to using of “natural surfactants”, peculiarly for domestic chemistry agents in the recent years. The term “natural surfactant” points to the natural origin of the compound. However, none of the presently used surfactants can be considered as natural completely. Except few examples all surfactants are produced via synthetic approaches often in the tough conditions following with formation of side products. For example, monoglycerides are widely spread in nature. But surfactants coming on the market as monoglycerides are received via industrial oil hydrolysis at the temperature higher than 200°C leading to side products formations. The alkylglycosides are extremely spread in living organisms but surfactants of this class are obtained via sequential chemical process and cannot be considered as natural. Among new types of surfactants the derivatives of natural amino acids should be underlined e.g. glycine derivatives - sodium laurylsarcosinate. There are only few reports in this area about the new surfactants of mixed types combining functions of ionogenic, nonionogenic and polyesterether surfactants based on the biocompatible nontoxic substances.

The concept of aminofunctional diesterethers integrates all unique properties of amino acids and polyesters: biocompatibility, chemical and structural versatility, biodegradation ability. Though there are not many successful researches in this area. According to this approach a lot of compounds with controllable properties can be synthesized [3, 4, 5]. Moreover, either amino group or carboxyl group or both in the molecules of aminofunctional esters can be modified or used for covalent grafting of functional fragments.

In addition polymers based on oxyethylene are allowed by The Food and Drug Administration to use in medicine, food products and cosmetics and have been successfully studied.

The combination of natural amino acids and polyoxyethylene in the molecules of amphiphilic diesters significantly expands the application range of these substances fulfilling increasing requirements to cosmetics components.

Purpose of the paper. The purpose of the paper is development of synthetic approach to surfactants with controllable structure and properties based on the natural raw materials applicable for cosmetics production as dispersed systems stabilizers.

Results and discussion. The surfactants were synthesized using L-glutamic acid (α-aminoglutaric acid) – natural dibasic amino acid. The diesterethers with two terminal carboxyl groups (fig.1) were synthesized according to the Brenner reaction between N-derivatives of glutamic acid (2-heptadecanoyl) pentanedioic acid (Glu-St) and polyetherdiols [6].

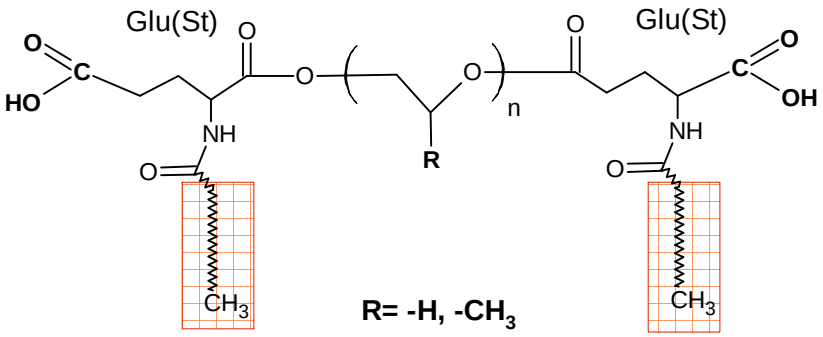

Fig.1. General structure of amphiphilic aminofunctional diesterethers.

These compounds possess surface-active properties and can be used as emulsifiers and dispersed systems stabilizers in the emulsion systems. The diesterethers can carry the wide range of functions – from oil-water to water-oil emulsifiers, dispersing agents, solubilizers of lipophilic substances in water medium – depending on the radical R and polyetherdiol fragment in their structure.

The clear cut distinction of aminofunctional diesterethers is presence of two carboxyl groups in the form of sodium salts. Therefore they can be considered as surfactants of mixed type. The molecules contain long-chain alkyl as pronounced lipophilic fragment and two ionogenic groups as hydrophilic fragment (fig.1). The polyoxyethylene and polyoxypropylene chains provide formation of sterically stabilized layers and improvement of solubilization and softness of cosmetic action.

As surface active properties assessment we choose ability to decrease surface tension and hydrophilic-lipophilic balance (HLB) as important criteria of compound applications for certain purposes. On the other hand surfactant characteristics using HLB values allow designing diesterethers with preselected properties.

To determine surface-active properties of synthesized diesterethers we conducted studies of surface tension change at different pH values of the medium according to the Du Noüy technique. The surface tension curves are presented on Fig. 2 and received characteristics for number of diesterethers - in Table 1. One can observe that all synthesized compounds decrease the surface tension to 33÷41mN/m fulfilling requirements to surfactants in cosmetic industry. The crucial micelle concentration (CMC) for these substances makes 0,005 ÷ 0,0075 wt. %.

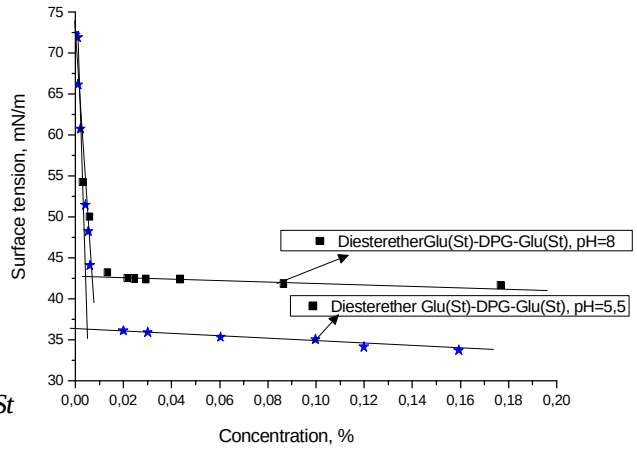

Fig. 2. Surface tension isotherms for Glu-St-DPG-Glu-St depending on pH of the medium.

The change of CMC values for synthesized diesterethers Glu-St-DPG-Glu-St and Glu-St-PEG400-Glu-St containing low lipophilic DPG and hydrophilic PEG400 depending on pH values of the medium is weakly pronounced. It allows expecting some stability of their properties in the cosmetic compositions for different applications.

Table 1

Characteristics of surface active properties of diesterethers depending on pH values of the medium

№	Substance	pH	CMC, %	σ_p, mN/m	HLB
1	Glu-St-DPG-Glu-St	5,5	0,0050	33,4	0,25
2	NaGlu-St-DPG-Glu-StNa	8	0,0075	41,8	34,25
3	Glu-St-PEG400-Glu-St	5,5	0,0059	34,5	3,65
4	NaGlu-St-PEG400-Glu-StNa	8	0,0072	34,1	38,4

The HLB values calculated according to the technique are presented in the table 1[6]. It demonstrates the significant effect of diesterether structure on HLB value. Paying attention to the research results and the latest publications we can conclude that synthesized diesterethers at low pH due to strong influence of lipophilic fragments and weak influence of hydrophilic fragments in molecules easily combine with oil phase and can be considered as stabilizers of reverse emulsion. Increasing of pH of solution leads to increasing of hydrophilic fragment effect since carboxyl groups in the form of alkali salts have group values exceeding effect of the lipophilic chains. Respectively at pH=8 diesterethers dissolve in water and decrease surface tension to 34÷41 mN/m and at high HLB values can function as stabilizers of oil/water emulsion.

The described aminofunctional diesterethers can offer the significant interest as surfactants for cosmetics production. The wide range of preselected properties allows the whole gamut of compositions for different applications. Depending on the HLB values and degree of carboxyl groups' neutralization the synthesized diesterethers can be used as stabilizers of direct and reverse emulsions in cosmetic and pharmaceutical industries.

It is well known that the most effective stabilizers for the dispersed systems are emulsifier's blends. Quantitative ratio of emulsifiers in the blend corresponds to the rule of additivity of HLB values. The rule of additivity of emulsifiers' HLB values consists in the following: $HLB_{oil} = W_a \times HLB_a + W_в \times HLB_в$ (HLB_{oil} – HLB value of stable emulsion, W_a and $W_в$ – mass part of emulsifiers "a" and "b" in the emulsifiers' blend, HLB_a and HLB_b – HBL values of emulsifiers "a" and "b". Monosodium salt of diesterether NaGluStPEG400GluSt (HLB=26,3) was used as emulsifier of the first kind, as emulsifier of the second kind – lipophilic diesterether GluStDPGGluSt (HLB=0,25). The olive oil with HLB value 10 was used for formation of direct emulsion.

The emulsifiers were taken in amounts to meet calculated HLB value of emulsion (HLB_{oil}) in the range 9,5÷10,5 (to form oil/water emulsion). The forerunning experiments established that out of this diapason stability of emulsions is insufficient and minimal amount of emulsifiers makes 3%.

Table 2

Results of studies of direct and reverse emulsions stabilized with diesterethers blend

№	Oil phase content (%)	Content of diesterether in emulsifiers' blend, %		HLB value of emulsifiers' blend	Total amount of emulsifiers, %	Delamination of emulsion after 7 days, %
		GluSt-DPG-GluSt	NaGluSt-PEG400-GluSt			
Oil/water emulsion						
1	50	65	35	9,5	3	20
2	50	63	37	10	3	2
3	50	61	39	10,5	3	0
Water/oil emulsion						
4	44	83	17	4,7	6	30
5	44	81	19	5,2	6	9
6	44	79	21	5,8	6	1

The emulsions were tested via dissolving of water- and oil-soluble dyes in emulsions. The conducted experiments demonstrates that samples 1-3 (table 2) are oil/water emulsions as water-soluble dye Malachite Green tinctures emulsion dispersed phase and oil-soluble dye only dispergates. On the contrary oil-soluble dye Sudan III tinctures emulsion dispersed phase of samples 4-6 as for water/oil emulsion.

Conclusions. Thus, the aminofunctional diesterethers can be applied as soft surfactants based on the natural raw materials for cosmetics production. The wide range of preselected properties allows developing the whole gamut of compositions for different applications.

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UDC 544.23; 621.315.616.97; 544.77

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POLYMER NANOCOMPOSITE FILMS EMBEDDED CARBON NANOTUBES

The conductive nanocomposite films on the basis of reactionary copolymers with embedded carbon nanotubes were received. The percolation threshold of obtained nanocomposites was determined and it was shown that its value depends on the size of specific surface of nanotubes, composition and conditions of composite obtaining.

Key words: reactionary copolymers, carbon nanotubes, conductive nanocomposites, percolation threshold.

Одержано струмопровідні нанокомпозитні плівки на основі реакційноздатних кополімерів з вбудованими вуглецевими нанотрубками. Визначено поріг перколяції одержаних нанокомпозитів і показано, що його значення залежить від величина питомої поверхні нанотрубок, складу та умов одержання композиту.

Ключові слова: реакційноздатні кополімери, вуглецеві нанотрубки, струмопровідні нанокомпозити, поріг перколяції.

Problem definition. With the development of technologies of the new nanofiller creation the possibility of receiving the polymer composite materials filled with carbon nanotubes (CNT) has attracted increasing attention. The CNT possess the unique gamut of specific properties – for example they can have metallic conductivity as well as be semiconductor or dielectric depending on their structure and