Influence of Different Catalysts and Solvents on the General Base Catalytical Esterification of Polyoxyethylene Sorbitan Trioleate with Maleic Anhydride and Styrene-Co-Maleic Anhydride

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Abstract

The general base catalitycal esterification of Polyoxyethylene sorbitane Trioleate with maleic anhydride (Ma) and styrene-co-maleic anhydride (Sma) using pyridine as catalyst is described. We investigated the effect of different factors on the yield of reaction product. The analysis of the effect of different factors on the process of catalytical esterification showed that the catalysts and solvents can be arranged by their activity in the following order: sulfuric acid > toluene sulfonic acid > triethylamine > pyridine > without a catalyst and dimethylsulfoxide (DMSO) > O-xylene > dimethylformamide (DMF), respectively. It should be noted that pyridine to its activity is not significantly inferior to the traditional catalysts and with DMSO using the yield of product is increasing. It is concluded that the reaction proceeds by 2nd order. It was found that decreasing the temperature of reaction to a lower temperature, where there is an intensive incubation period, leads to decreasing of yield of polyesters. The rate constant and activation energy were calculated. It was found that the process occurred on 98% at 130 °C and 80 minutes for PoesTo/Ma and on 88% at 150 °C and 40 minutes for PoesTo/Sma. For preparation of reaction product to analysis new methods were developed. It was shown, that on ^{1}H and ^{13}C spectra an overlap of the individual peaks or their close concentration in one area is observed, which makes it not possible to complete the analysis of the spectra. ^{1}H and ^{13}C spectra give a preliminary idea of the structure of the reaction products. It is concluded that 2-D NMR measurements more useful for further confirming of structure of PoesTo/Ma and PoesTo/Sma. HLB shown that we obtained two different surfactants where by catalytical esterification the hydrophilic part of Tween in PoesTo/Ma and the lipophilic part in PoesTo/Sma was increased.

Introduction

Developments of effective reagents for oil treatment are actual in oil-producing countries. Research to develop reagents involves the study of not only the structures and physical-chemical characteristics, but involves and kinetic calculations, describing the process of synthesis reagents depending on the chemical reaction.

Polyesters are one of the most versatile synthetic polymers. They are widely used in the manufacturing of pharmaceuticals, plasticizers, and as surfactants in the oil industries. Roodbari et al. [1] have reported that Tween-85 have demulsification effect on heavy crude oil/water emulsions. Furthermore, recent studies [2] took advantage of the use of Tween-85 as inhibition agent of the corrosion for cold rolled steel. It's known that in the oil industry is widely used surfactants. In the research work of

Singh Rajput and et al. [3] was shown that styrene-co-maleic anhydride has been used for the preparation of chemically and diffusionaly controlled polymeric prodrugs poly(sterene-co-maleic anhydride) conjugates with phenol based medicinal natural products. Lessard and Maric [4] have reported that styrene and maleic anhydride copolymers are widely used as polymer blend compatibilizers and adhesion promoters and that such functionalized block copolymers would be highly useful as surfactants and as possible precursors for in situ formation of melt-processed block copolymers or composites with nanometer scale morphologies.

Catalytical esterification is one of the most fundamental and important reactions in polymer chemistry. Examples of condensation polymers are polyamides, polyesters, phenolic resins, polyurethanes, etc. [5]. Strong liquid mineral acids, such as H_2SO_4, HCl, and HI are effective for the esterification of car-

boxylic acids. Well-known catalysts for esterification are p-toluene sulphonic acid and the salts of Ti(IV) and Sn(IV). It should be noted that a related catalyst [6], the $HfCl_4(THF)_2$ complex catalyzed the direct polycondensation of diols and dicarboxylic acid compounds, more efficiently than conventional catalysts. Recent esterification processes carry out with the use of mild catalysts, 4-(nitro)-diphenylammonium triflate [7] and diphenylammonium triflate [8].

Most classical scholars engaged in the study of kinetics and mechanism of catalytical esterification, base their work on the principle of equal reactivity of functional groups, regardless of the size of the molecule, to which they belong. According to this principle, each functional group reacts with another with at the same rate, regardless of whether this group belongs to a monomer or oligomer [9-13].

It should be noted that Flory [9,10] and Tang [11] and co-workers, who studied the kinetics of catalytical esterification in the absence and presence of the catalyst, established that in the absence of a catalyst, the reaction obeys the 3rd and $2^{0.5th}$ order, and in the presence of a catalyst − laws 2nd order (bimolecular mechanism). The mechanism and kinetics of catalytical esterification have been investigated in the past as well as today [14-17].

Here we report the preparation of novel polyesters, their characterization with ^1H, ^{13}C, 2-D COSY and HSQC NMR, and investigation of the influence of different catalysts and solvents on the yields of polyesters. Newly prepared polyesters with adjustable hydrophilic–hydrophobic balance and high oil solubility were synthesized by one-step catalitycal esterification of readily available and non-corrosion active components: Polyoxyet hylene sorbitane Trioleate (PoesTo or Tween-85), maleic anhydride (Ma) or styrene-co-maleic anhydride (Sma), pyridine as catalyst and dimethylsulfoxide (DMSO) as solvent. Due to the presence of a carboxyl group we can further adjust HLB through additional step of catalytical esterification of prepared polyesters with matching alcohol in one reactor. The ability to control the HLB of polyesters opens exciting opportunities for practical applications in industries such as oilfield chemistry.

The Experiment

Materials and Methods

All reagents manufactured by Aldrich were used without additional purification. COSY and HSQC NMR spectra were obtained in deuterated dimethylsulfoxide with Bruker Avance-3-400 device. For column chromatography used silica with pore size 60A, 70-230 mesh, 63-200 μm.

Synthesis of PoesTo/Ma and PoesTo/Sma

The reaction takes place in three-necked flask which is equipped with a stirrer, a reflux condenser, a thermometer, and connecting pipe to enter the catalyst, solvent and diluent. 0.001 mole of Polyoxyethylene sorbitan Trioleate (Tween-85) was dissolved in 0.001 mole of dimethylsulfoxide. 0.001 mole of pyridine catalyst was injected into the reaction flask. In this stage pyridine forms an active complex with Tween-85. Then 0.001 mole of maleic anhydride or styrene-co-maleic anhydride was gradually added to the flask through the connecting pipe. The molar ratio of maleic anhydride and Tween-85 was 1:1. Then the temperature was raised to 100-150 °C and this temperature was maintained for 40-80 minutes with constant stirring and temperature control. Solvent vapors were trapped in a condenser (refrigerator) and poured back into the flask.

Preparation of PoesTo/Ma for analysis

To obtain the pure product of the reaction the solvent was founded and the method of thin layer chromatography, with the aim of further purification of the product from the impurities in the column chromatography, was used. For TLC was found the system acetonitrile-acetone in a ratio of 7.5/2.5. Identification of maleic anhydride and pyridine on a plate of silica was carried out under ultraviolet light. PoesTo/Ma and impurities of Tween-85 were identified in the cell with vapor of iodine as in the work of Katic and et al [18]. The solvent was removed by vacuum-rotary evaporator until the weight was constant.

Preparation of PoesTo/SMa for analysis

To obtain the pure product of the reaction method of precipitation were used. For quantitative precipitation of the non-reaction styrene-co-maleic anhydride was chosen methanol as in the work of Bonilla-Cruz and et al [19] and De Brouwer and et al. [20]. Then solution was decanting to other flask and removed in vacuum-rotary evaporator until the weight was constant. For the 2nd stage of precipitation of PoesTo/Sma was chosen diethyl ether. The precipitated polyester was dried by vacuum-rotary evaporator until the weight was constant.

Results and Discussion

Kinetics of the synthesis PoesTo/Ma and PoesTo/Sma

Fig. 1. shows the curves of dependence of the yield of PoesTo/Ma from time in the temperature range 100-130 °C. The yield of the product after 80 minutes at 100 °C is 92.6%, 95% at 110°C, 96.7%

at 120 °C, and 98% at 130 °C. The reaction slows down after 80 minutes. It was found that a further increase in the reaction time up to 4 hours does not significantly influence to the escape depth of the re-action product and the yield of PoesTo/Ma was 96% for 100 °C, 97.8% for 110 °C, 98% for 120 °C, and 99% for 130 °C.
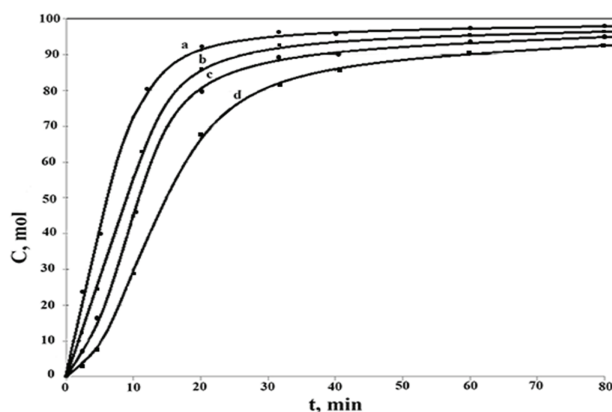

Fig. 1. Dependence of the yield of the PoesTo/Ma with time at 130 °C (a), 120 °C (b), 110 °C (c) and 100 °C (d).

Fig. 2. shows the curves of dependence of the yield of PoesTo/Sma from time in the temperature range 130-150 °C. The yield of the product after 120 minutes at 130 °C is 2.9%, 71.43% at 13 5 °C, 85.3% at 140 °C, and 88% at 150 °C. The reaction slows down after 120 minutes at 130 °C, 200 min-utes at 135 °C, 120 minutes at 140 °C and 40 min-utes at 150 °C. It was found that a further increase in the reaction time up to 4 hours does not significantly influence to the escape depth of the reaction product and the yield of PoesTo/Sma was 2.9% for 130 °C, 81.5% for 135 °C, 85.3% for 140 °C, and 88% for 150 °C.
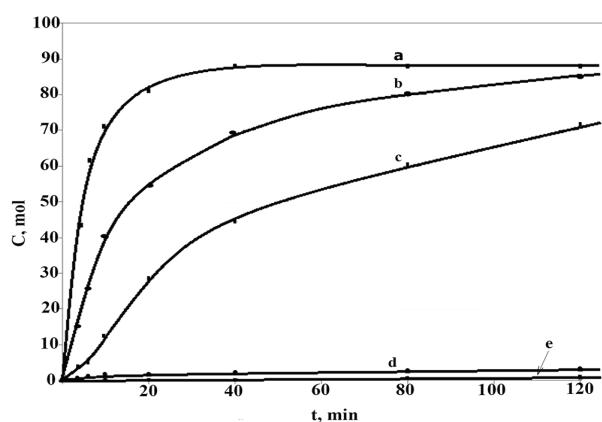

Fig. 2. Dependence of the yield of the PoesTo/SMa with time at 150 °C (a), 140 °C (b), 135 °C (c), 130 °C (d) and 120 °C (e).

In the 0 to 10 minutes an incubation period can be seen, the intensity of which decreases as the temperature increases. It was found that decreas-ing the temperature of the catalytical esterification of Tween-85 with maleic anhydride and styrene-co-maleic anhydride to a lower temperature, where there is an intensive incubation period, is impracti-cal because, in this temperature range, a decrease in the yield of PoesTo/Ma and PoesTo/Sma are seen.

Since the initial concentration of the reactants is equal, the following equation was used to describe the rate:

$$dx/dt=k_r dt \qquad (1)$$ or

$$dx/(a-x)2=k_r dt \qquad (2).$$

After integration was obtained

$$k_r dt=1/(a-x) + const \qquad (3),$$

where const−constant of integration.

Having analyzed of data, it was concluded that the catalytic esterification of Tween-85 with maleic anhydride and styrene-co-maleic anhydride in the presence of pyridine proceeds by 2nd order. It was calculated that the reaction rate constant for PoesTo/Ma at 100 °C is equal to 0.3640 $dm^{-3} \cdot mol^{-1} \cdot min^{-1}$, at 110 °C $k_r = 0.5543$ $dm^{-3} \cdot mol^{-1} \cdot min^{-1}$, at 120 °C $k_r = 0.8390$ $dm^{-3} \cdot mol^{-1} \cdot min^{-1}$, at 130 °C $k_r = 1.3270$ $dm^{-3} \cdot mol^{-1} \cdot min^{-1}$ and for PoesTo/Sma at 130 °C is equal to 0.0175 $dm^{-3} \cdot mol^{-1} \cdot min^{-1}$, at 135 ºC $k_r = 0.04$ $dm^{-3} \cdot mol^{-1} \cdot min^{-1}$, at 140 °C $k_r = 0.097$ $dm^{-3} \cdot mol^{-1} \cdot min^{-1}$, at 150 °C $k_r = 0.325$ $dm^{-3} \cdot mol^{-1} \cdot min^{-1}$.

From the Arrhenius Equation it is possible to de-termine the activation energy.

$$k_r = A\exp(-E^{\#}/RT) \qquad (4),$$

where T stands for temperature (in absolute tem-perature kelvin), A is the pre-exponential factor, R is the Universal gas constant, $E^{\#}$ - activation energy, J/mol or kcal/mol.

The logarithmic form of the equation is:

$$\ln k_r = \ln A - E^{\#}/RT \qquad (5)$$ or

$$\lg k_r = \lg A - E^{\#}/2.303RT \qquad (6).$$

It was calculated that the activation energy of synthesis of PoesTo/Ma is 25.5 kcal/mol[-1] and 98.8 kcal/mol[-1] for PoesTo/SMa.

Therefore, it has been suggested that the optimal synthesis conditions of reagent PoesTo/Ma is 130 ºC for 80 minutes and PoesTo/SMa is 150 °C for 40 minutes.

The effect of different catalysts on the process of catalytical esterification of Tween-85 with maleic anhydride and styrene-co-maleic anhydride were analyzed. Data for the study of the effect of different catalysts is shown in Table 1. The results showed that the catalysts can be arranged by their activity in the following order: sulfuric acid > toluene sulfonic acid > triethylamine > pyridine > without a catalyst. The most active catalyst of the process is sulfuric acid, but sulfuric acids possess highly corrosive activity to equipment. Triethylamine is corrosive to aluminum, zinc, copper and their alloys in the presence of moisture, and for some types of plastic and rubber. Pyridine as catalyst is more usable for this process because for industrial experiments we are going to use the reaction solution as a demulsifier and depressor.

Table 1
The effect of different catalysts on the yield of reaction product

Catalyst	$t_{(PoesTo/Ma)}/$ $t_{(PoesTo/Sma)}$, min	$T_{(PoesTo/Ma)}/$ $T_{(PoesTo/Sma)}$,°C	$\eta_{(PoesTo/Ma)}/$ $\eta_{(PoesTo/Sma)}$, %
without a catalyst	80/40	130/150	47.2/30
H_2SO_4	80/40	130/150	99/96
CH_3C_6 H_4SO_2OH	80/40	130/150	98.5/92
$N(C_2H_5)_3$	80/40	130/150	98/90
NC_5H_5	80/40	130/150	98/88

The effect of different solvents on the process of catalytical esterification of Tween-85 with maleic anhydride and styrene-co-maleic anhydride are shown in Table 2. The results showed that the solvents can be arranged by their activity in the following order: dimethylsulfoxide (DMSO) > O-xylene > dimethylformamide (DMF). The most usable solvent of the process is DMSO, because with his using the yield of product is increasing. It should be noted that the direct dependence of degree of modifications of styrene-co-maleic anhydride and maleic anhydride from basicity and dielectric constant was not found.

Table 2
The effect of different solvents on the process of catalytical esterification

Solvent	$T_{b.p.}$,°C	Reaction time, min	$\eta_{(PoesTo/Ma)}$ at 130 C, %	$\eta_{(PoesTo/Sma)}$ at 140 C, %
DMSO	189	240	99	85.3
O-xylene	144	240	90	74
DMF	153	240	78	64

Characterization of PoesTo/Ma and PoesTo/Sma

To gain insight into the chemical composition of PoesTo/Ma and PoesTo/Sma, modified surfactants was analyzed using NMR spectrometry. The ^{1}H NMR spectrum of PoesTo/Ma is shown in Fig. 3. (see appendices), where the peak at $\delta = 4.17$ ppm (m) may be assigned to $-CH_2-O-C(O)-C-$ in the formation ester group and $\delta = 6.3$ ppm (g) is attributed to two methylene protons in $-(-OOC)HC=CH(COO-)-$. The ^{1}H NMR spectrum of PoesTo/Sma is shown in Fig. 4. (see appendices), where the peak at $\delta = 4.17$ ppm (m) may be assigned to $-CH_2-O-C(O)-C-$ in the formation ester group and $\delta = 2.58$ ppm (g) is attributed to two methylene protons in $-(-OOC)HC-CH(COO-)-$.
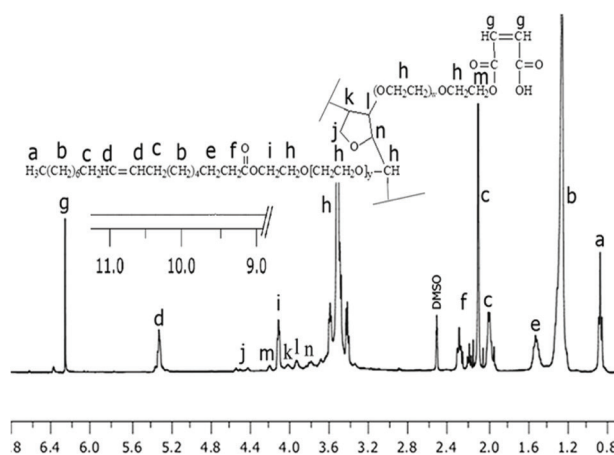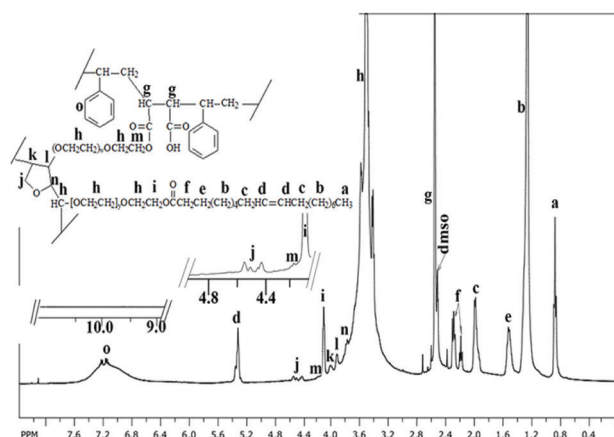

Fig. 3. ^{1}H NMR spectra of PoesTo/Ma.

Fig. 4. 1H NMR spectra of PoesTo/Sma

In the ^{13}C NMR spectrum of PoesTo/Ma (Fig. 5, see appendices) band at $\delta = 65$ ppm (m) is attributed

to -C-O-C- and band at δ = 168 ppm (r) to C = O in formation ester group. The band at δ = 205 ppm (q) is attributed to the C = O bonds in the carboxylic group. The peak at δ = 132 ppm (g)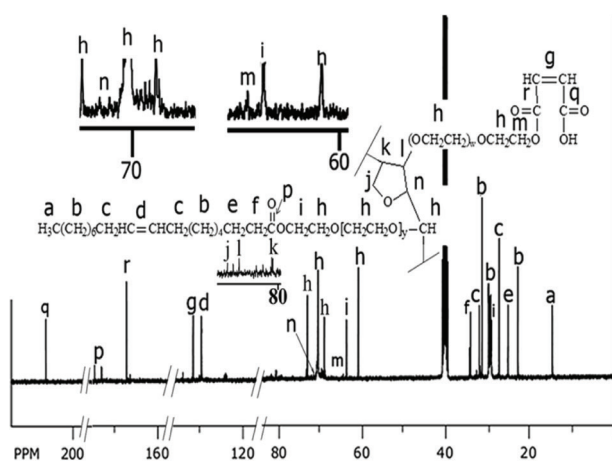 is attributed to the –HC=CH– bonds in -(-OOC)HC =CH(COO-)-. In the ¹³C NMR spectrum of PoesTo/Sma (Fig. 6, see appendices) band at δ = 61 ppm (m) is attributed to -C-O-C- and band at δ = 163.5 ppm (p) to C = O in formation ester group. The band at δ = 205 ppm (r) is attributed to the C = O bonds in the carboxylic group. The peak at δ = 41.5 ppm (g) is attributed to the –HC-CH– bonds in -(-OOC)HC-CH(COO-)-.

Fig. 5. ¹³C NMR spectra of PoesTo/Ma.
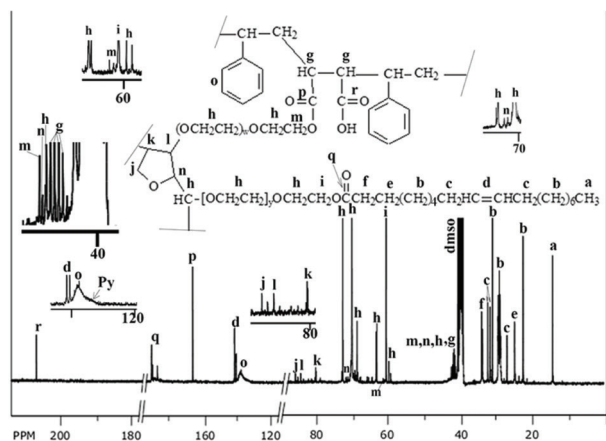
Fig. 6. ¹³C NMR spectra of PoesTo/Sma.

As PoesTo/Ma and PoesTo/Sma are a high molecular compounds, on the ¹H NMR and ¹³C NMR an overlap of the individual peaks or their close concentration in one area is observed, which makes it not possible to complete the analysis of the spectra.

The structure of PoesTo/Ma and PoesTo/Sma was further confirmed with 2-D NMR measure-

ments. COSY spectra of PoesTo/Ma and Poesto/Sma are shown in Figs. 7. and Fig. 8., respectively. In the both 2D COSY spectrums the order of the methyl and methylene groups in the structure of PoesTo/Ma and PoesTo/Sma was found.
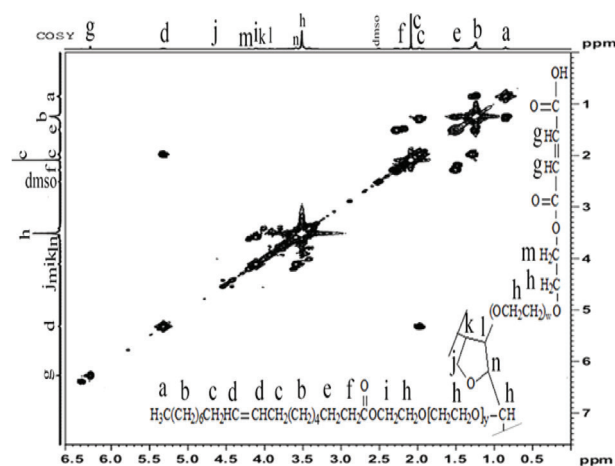

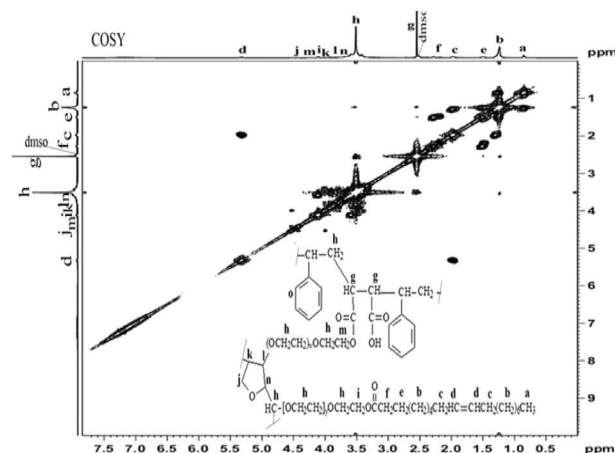Fig. 7. 2D COSY spectra of PoesTo/Ma.

Fig. 8. 2D COSY spectra of PoesTo/Sma.

The COSY spectra of PoesTo/Ma assisted in confirming the assignment of CH₃ groups of oleic part of molecule at 0.85 ppm (a) that correlate with the neighboring CH₂ groups at 1.24 ppm (b). In turn, CH₂ groups at 1.24 ppm (b) give cross peak with the neighboring CH₂ units (c) at 1.98 and 2.087 ppm, and with the neighboring CH₂ unit (e) at 1.51 ppm. CH₂ unit (e) at 1.51 ppm correlates with the neighboring CH₂ group (f), which peak corresponds to 2.18 and 2.19 ppm. CH₂ units (c) at 1.98 and 2.087 ppm give cross peak with the neighboring methylene groups in –HC=CH– bond in oleic part of molecule at 5.3 ppm (d). Peak at 4.4-4.54 ppm (j) which at-

tributed to methylene group in –HC–O–CH– in oxygen-containing heterocyclic ring correlate with the neighboring methylene group at 4.01 ppm (k). Then, methylene group at 4.01 ppm (k) correlate with the neighboring methylene group at 3.93 ppm (l). Methylene group at 3.93 ppm (l) forms cross peak with the neighboring methylene group in –HC–O–CH– in oxygen-containing heterocyclic ring, which located at 3.78 ppm (n). In turn, methylene group at 3.78 ppm (n) correlate with the neighboring methylene groups at 3.5-3.6 ppm (h). It was found that CH_2 groups of -CH_2-O-C(O)-C- in the formation ester group (4.17 ppm, m) correlate with the neighboring CH_2 group in -CH_2-O-CH_2- in polyoxyethylene moiety (3.5-3.6 ppm, h). CH_2 group in -CH_2-O-CH_2- in polyoxyethylene moiety at 3.5-3.6 ppm (h) give cross peak with the neighboring CH_2 unit at 4.11 ppm (i).

From the COSY spectra of PoesTo/Sma was found that CH_3 groups of oleic part of molecule at 0.85 ppm (a) that correlate with the neighboring CH_2 groups at 1.238 ppm (b). CH_2 groups at 1.238 ppm (b) give cross peak with the neighboring CH_2 units (c) at 1.97 ppm, and with the neighboring CH_2 unit (e) at 1.5 ppm. In turn, CH_2 unit (e) at 1.5 ppm correlates with the neighboring CH_2 group (f), which peak corresponds to 2.17 and 2.29 ppm. CH_2 units (c) at 1.97 ppm give cross peak with the neighboring methylene groups in –HC=CH– bond in oleic part of molecule at 5.3 ppm (d). Peak at 4.41-4.53 ppm (j) which attributed to methylene group in –HC–O–CH– in oxygen-containing heterocyclic ring correlate with the neighboring methylene group at 4.016 ppm (k). Then, methylene group at 4.016 ppm (k) correlate with the neighboring methylene group at 3.92 ppm (l). Methylene group at 3.92 ppm (l) forms cross peak with the neighboring methylene group in –HC–O–CH– in oxygen-containing heterocyclic ring, which located at 3.777 ppm (n). Methylene group at 3.777 ppm (n) correlate with the neighboring methylene groups at 3.5-3.6 ppm (h). It was found that CH_2 groups of -CH_2-O-C(O)-C- in the formation ester group (4.17 ppm, m) correlate with the neighboring CH_2 group in -CH_2-O-CH_2- in polyoxyethylene moiety (3.5-3.6 ppm, h). CH_2 group in -CH_2-O-CH_2- in polyoxyethylene moiety at 3.5-3.6 ppm (h) give cross peak with the neighboring CH_2 unit at 4.11 ppm (i) and with the neighboring methylene group in –HC-CH– bond in formation ester group at 2.58 ppm (g).

It should be noted that cross peaks formed by 2.58 ppm with 1.238 ppm, 2.58 ppm with 1.5 ppm and 3.5-3.6 ppm with 1.238 ppm are quantitative reflections and other artifacts.

HSQC spectra of PoesTo/Ma and PoesTo/Sma are shown in Figs. 9. and Fig. 10., respectively. Analysis of main cross peaks in HSQC spectra of

PoesTo/Ma concluded that bands at δ = 6.3 ppm correlate with peak at δ = 132 and forming cross peak (g), which attributed to methylene group in –HC=CH– bond in the formation ester group. It was found that peak at δ = 5.3 ppm correlate δ = 130 ppm, and give cross peak (d) which related to the methylene groups of -HC=CH- bonds in the oleic moiety. Cross peak (m) which forming by peaks at δ = 4.17 ppm and δ = 65 ppm belongs to methylene group in -CH_2-O-C(O)-C- bond in the formation ester group.
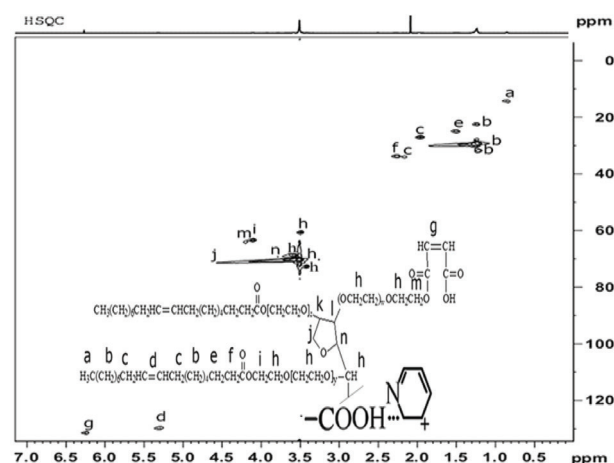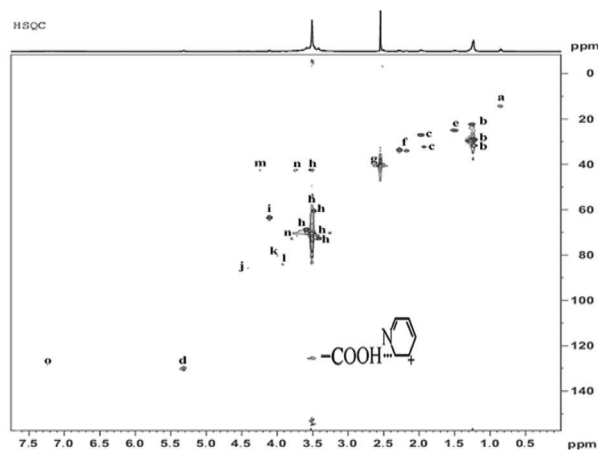

Fig. 9. HSQC spectra of PoesTo/Ma.

Fig. 10. HSQC spectra of PoesTo/Sma.

In the HSQC spectra of PoesTo/Sma bands at δ = 2.58 ppm correlate with peak at δ = 41.5 and forming cross peak (g), which attributed to methylene group in –HC-CH– bond in the formation ester group. Peak at δ = 5.3 ppm correlate δ = 130 ppm, and give cross peak (d) which related to the methylene groups of -HC=CH- bonds in the oleic moiety.

Cross peak (m) which forming by peaks at $\delta = 4.17$ ppm and $\delta = 41.55$ ppm belongs to hydrocarbon bond of second methylene group in -CH$_2$-CH$_2$-O-C(O)-C- bond in the formation ester group.

The main physical-chemical characteristics of surfactants are shown in Table 3, where HLB was determined by Griffin's method. Data of studies are shown that we obtained two different surfactants. By catalytical esterification the hydrophilic part of Tween in PoesTo/Ma and the lipophilic part in PoesTo/Sma were increased. Both surfactants are soluble in oil and dispergate in water. HLB of PoesTo/Ma is 13 and remains stable, because the degree of modification of the polyester reaches almost 99%, whereas HLB of PoesTo/Sma in depending on the degree of modification can reach a value from 8 to 11.5. This is due to the fact that the maximum modification of PoesTo/Sma passes on 88%.

Table 3
Physical-chemical characteristics of surfactants

Sample	Mw surfactant	HLB	Solubility	
			Oil	Water
Tween-85	1836.6	11	Soluble	Dispergate
PoesTo/Ma	1934	13	Soluble	Dispergate
PoesTo/Ma	2038	8-11.5	Soluble	Dispergate

Conclusion

In this paper, the effectiveness of pyridine as a catalyst and DMSO as a solvent for general base catalytical esterification was studied. Different types of surfactants were synthesized by using pyridine catalyst. It was studied that the catalysts and solvents can be arranged by their activity in the following order: sulfuric acid > toluene sulfonic acid > triethylamine > pyridine > without a catalyst and DMSO > O-xylene > DMF, respectively. The structure of polyesters was studied and proven by NMR. By catalytical esterification the hydrophilic part in PoesTo/Ma and the lipophilic part in PoesTo/Sma were increased. The process occurred on 98% at 130 °C and 80 minutes for PoesTo/Ma and on 88% at 150 °C and 40 minutes for PoesTo/Sma. The advantage of pyridine as the base catalyst lies in the fact that it shows non-corrosion activity.

Acknowledgements

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