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

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Abstract
The general base catalytic 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 catalytic 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 1H and 13C 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. 1H and 13C 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 treatments 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(stereone-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 H2SO4, HCl, and HI are effective for the esterification of car-
boxylic acids. Well-known catalysts for esterification are p-toluene sulphonylic acid and the salts of Ti(IV) and Sn(IV). It should be noted that a related catalyst [6], the HfCl₄(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 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, 13C, 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 catalytical esterification of readily available and non-corrosion active components: Polyoxyethyl hydylene 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 Polyoxymethylene sorbitane 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 reaction 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.

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 decreasing 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 impractical 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:

\[
\frac{dx}{dt} = k_r t
\]

or

\[
\frac{dx}{(a-x)^2} = k_r t
\]

After integration was obtained

\[
k_r t = \frac{1}{(a-x)} + \text{const}
\]

where \text{const} = \text{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$^{-3}$·mol$^{-1}$·min$^{-1}$, at 110 °C $k_r = 0.5543$ dm$^{-3}$·mol$^{-1}$·min$^{-1}$, at 120 °C $k_r = 0.8390$ dm$^{-3}$·mol$^{-1}$·min$^{-1}$, at 130 °C $k_r = 1.3270$ dm$^{-3}$·mol$^{-1}$·min$^{-1}$ and for PoesTo/Sma at 130 °C is equal to 0.0175 dm$^{-3}$·mol$^{-1}$·min$^{-1}$, at 135 °C $k_r = 0.04$ dm$^{-3}$·mol$^{-1}$·min$^{-1}$, at 140 °C $k_r = 0.097$ dm$^{-3}$·mol$^{-1}$·min$^{-1}$, at 150 °C $k_r = 0.325$ dm$^{-3}$·mol$^{-1}$·min$^{-1}$.

From the Arrhenius Equation it is possible to determine the activation energy:

\[
k_r = A \exp\left(-\frac{E^*}{RT}\right)
\]

where $T$ stands for temperature (in absolute temperature 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:

\[
\ln k_r = \ln A - \frac{E^*}{RT}
\]

or

\[
\lg k_r = \lg A - \frac{E^*}{2.303RT}
\]

It was calculated that the activation energy of synthesis of PoesTo/Ma is 25.5 kcal/mol and 98.8 kcal/mol for PoesTo/Sma.

Therefore, it has been suggested that the optimal synthesis conditions of reagent PoesTo/Ma is 130 °C 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       | $\frac{t(\text{PoesTo/Ma})}{t(\text{PoesTo/Sma})}$, % | $\frac{T(\text{PoesTo/Ma})}{T(\text{PoesTo/Sma})}$, ºC | $\frac{\eta(\text{PoesTo/Ma})}{\eta(\text{PoesTo/Sma})}$, % |
|----------------|---------------------------------------------------|--------------------------------------------------|---------------------------------------------------|
| without a catalyst | 80/40                                           | 130/150                                         | 47.2/30                                           |
| H$_2$SO$_4$     | 80/40                                           | 130/150                                         | 99/96                                            |
| CH$_3$C$_6$H$_4$SO$_2$OH | 80/40                                       | 130/150                                         | 98.5/92                                          |
| N(C$_2$H$_5$)$_3$ | 80/40                                           | 130/150                                         | 98/90                                            |
| NC$_5$H$_5$     | 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        | $T_b$, ºC | Reaction time, min | $\eta(\text{PoesTo/Ma})$ at 130 ºC, % | $\eta(\text{PoesTo/Sma})$ at 140 ºC, % |
|----------------|-----------|--------------------|--------------------------------------|--------------------------------------|
| 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.](image-1)

![Fig. 4. $^1$H NMR spectra of PoesTo/Sma.](image-2)
to \(-\text{C-O-C}\)- and band at \(\delta = 168\) ppm (r) to \(\text{C} = \text{O}\) in formation ester group. The band at \(\delta = 205\) ppm (q) is attributed to the \(-\text{HC} = \text{CH}\)- bonds in \(-\text{OOOC}\text{HC} = \text{CH}(-\text{COO}^-)\). In the \(^{13}\text{C}\) NMR spectrum of PoesTo/Sma (Fig. 6, see appendices) band at \(\delta = 61\) ppm (m) is attributed to \(-\text{C-O-C}\)- and band at \(\delta = 163.5\) ppm (p) to \(\text{C} = \text{O}\) in formation ester group. The band at \(\delta = 205\) ppm (r) is attributed to the \(\text{C} = \text{O}\) bonds in the carboxylic group. The peak at \(\delta = 41.5\) ppm (g) is attributed to the \(-\text{HC} = \text{CH}\)- bonds in \(-\text{OOOC}\text{HC} = \text{CH}(-\text{COO}^-)\).

**Fig. 5.** \(^{13}\text{C}\) NMR spectra of PoesTo/Ma.

**Fig. 6.** \(^{13}\text{C}\) NMR spectra of PoesTo/Sma.

As PoesTo/Ma and PoesTo/Sma are a high molecular compounds, on the \(^1\text{H}\) NMR and \(^{13}\text{C}\) 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 measurements. 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 \(\text{CH}_3\) groups of oleic part of molecule at 0.85 ppm (a) that correlate with the neighboring \(\text{CH}_2\) groups at 1.24 ppm (b). In turn, \(\text{CH}_3\) groups at 1.24 ppm (b) give cross peak with the neighboring \(\text{CH}_2\) units (c) at 1.98 and 2.087 ppm, and with the neighboring \(\text{CH}_2\) unit (e) at 1.51 ppm. \(\text{CH}_2\) unit (e) at 1.51 ppm correlates with the neighboring \(\text{CH}_2\) group (f), which peak corresponds to 2.18 and 2.19 ppm. \(\text{CH}_2\) units (c) at 1.98 and 2.087 ppm give cross peak with the neighboring methylene groups in \(-\text{HC} = \text{CH}\)- 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 \(-\text{HC}–\text{O–CH–}\) 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 \(-\text{HC}–\text{O–CH–}\) 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 \(\text{CH}_2\) groups of -\(\text{CH}_2\)-\(\text{O–C(O)}\)-\(\text{C–}\) in the formation ester group (4.17 ppm, m) correlate with the neighboring \(\text{CH}_2\) group in -\(\text{CH}_2\)-\(\text{O–CH}_2\) in polyoxyethylene moiety at 3.5-3.6 ppm (h) give cross peak with the neighboring \(\text{CH}_2\) unit at 4.11 ppm (i).

From the COSY spectra of PoesTo/Sma was found that \(\text{CH}_3\) groups of oleic part of molecule at 0.85 ppm (a) that correlate with the neighboring \(\text{CH}_2\) groups at 1.238 ppm (b). \(\text{CH}_2\) groups at 1.238 ppm (b) give cross peak with the neighboring \(\text{CH}_2\) units (c) at 1.97 ppm, and with the neighboring \(\text{CH}_2\) unit (e) at 1.5 ppm. In turn, \(\text{CH}_2\) unit (e) at 1.5 ppm correlates with the neighboring \(\text{CH}_2\) group (f), which peak corresponds to 2.17 and 2.29 ppm. \(\text{CH}_2\) units (c) at 1.97 ppm give cross peak with the neighboring methylene groups in \(-\text{HC}–\text{CH–}\) 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 \(-\text{HC}–\text{O–CH–}\) 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 \(-\text{HC}–\text{O–CH–}\) 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 \(\text{CH}_2\) groups of -\(\text{CH}_2\)-\(\text{O–C(O)}\)-\(\text{C–}\) in the formation ester group (4.17 ppm, m) correlate with the neighboring \(\text{CH}_2\) group in -\(\text{CH}_2\)-\(\text{O–CH}_2\) in polyoxyethylene moiety (3.5-3.6 ppm, h). \(\text{CH}_2\) group in -\(\text{CH}_2\)-\(\text{O–CH}_2\) in polyoxyethylene moiety at 3.5-3.6 ppm (h) give cross peak with the neighboring \(\text{CH}_2\) unit at 4.11 ppm (i) and with the neighboring methylene group in \(-\text{HC}–\text{CH–}\) 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 \(\delta = 6.3\) ppm correlate with peak at \(\delta = 132\) and forming cross peak (g), which attributed to methylene group in \(-\text{HC}–\text{C}–\) bond in the formation ester group. It was found that peak at \(\delta = 5.3\) ppm correlate \(\delta = 130\) ppm, and give cross peak (d) which related to the methylene groups of \(-\text{HC}–\text{CH–}\) bonds in the oleic moiety. Cross peak (m) which forming by peaks at \(\delta = 4.17\) ppm and \(\delta = 65\) ppm belongs to methylene group in -\(\text{CH}_2\)-\(\text{O–C(O)}\)-\(\text{C–}\) bond in the formation ester group.

In the HSQC spectra of PoesTo/Sma bands at \(\delta = 2.58\) ppm correlate with peak at \(\delta = 41.5\) and forming cross peak (g), which attributed to methylene group in \(-\text{HC}–\text{CH–}\) bond in the formation ester group. Peak at \(\delta = 5.3\) ppm correlate \(\delta = 130\) ppm, and give cross peak (d) which related to the methylene groups of \(-\text{HC}–\text{CH–}\) 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 $-\text{CH}_2\text{-CH}_2\text{-O-}$ 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 dispersate 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  | Solubility Water |
|--------------|---------------|-----|-----------------|-----------------|
| Tween-85     | 1836.6        | 11  | Soluble         | Dispergate      |
| PoesTo/Ma    | 1934          | 13  | Soluble         | Dispergate      |
| PoesTo/Sma   | 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.

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