

Group selectivity of ethoxylation of hydroxy acids

ANTHONY J. O'LENICK, JR., and JEFF K. PARKINSON,
Siltech Inc., 4437 Park Drive, Norcross, GA 30093.

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Synopsis

A study of the ethoxylation of two hydroxy acids was undertaken to determine if there was any group selectivity of ethoxylation. The hydroxy acids chosen for study were 12-hydroxystearic and lactic acid. Standard ethoxylation reactions were carried out using one mole of ethylene oxide to one mole of each hydroxy acid.

Unlike typical fatty acids or alcohols, 12-hydroxystearic acid and lactic acid both ethoxylate without a catalyst. This could be explained by the presence of both a hydroxyl and carboxyl in the reaction solution or the presence of both groups in the same molecule. We suggest that this may be due to some type of complex forming between the oxide and the carboxyl and hydroxyl groups, since blends of stearic acid and stearyl alcohol fail to ethoxylate without a catalyst.

Despite the fact that carboxyl groups of the hydroxy acids studied ethoxylate almost exclusively under base catalyst, and predominately with no catalyst, the reaction rate does not show an induction period, which would be expected for carboxyl group ethoxylation. The ethoxylation rates approximate those of primary alcohols under base catalyst.

Ethoxylation of both hydroxyl groups and carboxyl groups has been practiced for many years in the preparation of many surface-active agents. Fatty acid ethoxylates and fatty alcohol ethoxylates are members of a wide range of ethoxylates that are excellent surfactants. Surfactants are surface-active agents that function as detergents, wetting agents, and emulsifiers. They are used as solubilizers, coupling agents, fiber lubricants, antistats, leveling agents, and dyeing assists (1). In addition, these materials are used in numerous personal care applications and are key raw materials in the preparation of other surfactants like fatty alcohol ether sulfates.

Ethylene oxide reacts in an extremely exothermic manner with compounds having a labile hydrogen. Fatty acids and fatty alcohols are two of many such compounds containing a labile hydrogen. Alkaline and acidic catalysts make the reaction possible and accelerate it.

FATTY ALCOHOL ETHOXYLATION

Fatty alcohols react with ethylene oxide at the hydroxyl group to give an ether linkage and a new hydroxyl group. While conceptually the reaction is simple, the reality is that the reaction product is a complex mixture of oligomeric products that are a series of compounds that contain different amounts of ethylene oxide (2). A relatively wide distribution of species that have varying amounts of oxide reaction products present on the base hydrophobe is produced by the reaction.

Our analyses of the products that are produced when one mole of ethylene oxide is reacted with one mole of stearyl and coco alcohol are shown in Tables I and II, respectively. The analyses were done via gas-liquid chromatography.

Table I shows that when one mole of ethylene oxide is reacted with one mole of fatty alcohol, adducts having no added ethylene oxide are the predominate material in the mixture, making up 60.3% of the mixture. The other adducts, ranging from 1 to 8 moles of ethylene oxide, make up the remainder. If the amount of ethylene oxide found on each adduct is multiplied by the percentage of that adduct, the EO contribution is calculated. The difference between the observed 0.978 moles and the 1.0 added is primarily polyoxyalkylene glycol formation.

Table II shows that when one mole of ethylene oxide is reacted with one mole of coco fatty alcohol, adducts having no added ethylene oxide are the predominate material in the mixture, making up 54.8% of the mixture. The other adducts, ranging from 1 to 8 moles of ethylene oxide, make up the remainder. If the amount of ethylene oxide found on each adduct is multiplied by the percentage of that adduct, the EO contribution is calculated. The difference between the observed 0.993 moles and the 1.0 added primarily represents polyoxyalkylene glycol formation.

Much work has been done in recent years to "peak" ethoxylates (3-6). Catalysts are chosen to produce peaked ethoxylates that have a more narrow distribution of ethoxylated oligomers.

Some excellent pioneering work in ethoxylation of fatty acids and fatty alcohols was published in 1956 by Wrigley *et al.* (7). This work indicated two salient properties of ethoxylation of alcoholic hydroxyl groups. First, the products of the reaction sequence are complex mixtures, and second, the reaction begins immediately; that is, there is no induction period prior to the start of the reaction. Induction time, as will be shown subsequently, is a salient property of fatty acid ethoxylation.

Figure 1 shows the number of moles of ethylene oxide that react with stearic acid and stearyl alcohol, using 0.5% KOH at 160 C. Clearly, there is a significant difference in the kinetics of ethoxylation comparing fatty acid ethoxylation and fatty alcohol ethoxylation. The differences are most dramatic in the initial stages of the reaction.

Table I
Ethoxylation of Stearyl Alcohol With One Mole Ethylene Oxide

Designation	Moles of EO [Value A]	Area % [Value B]	EO Contribution [Value (A) (B)]
18-0	0	60.3	0.000
18-1	1	13.6	0.136
18-2	2	8.8	0.176
18-3	3	7.9	0.237
18-4	4	5.9	0.236
18-5	5	2.2	0.110
18-6	6	0.9	0.054
18-7	7	0.3	0.021
18-8	8	0.1	0.008
	Total	100.0%	
	Total calculated moles added		0.978

Table II
Ethoxylation of Coco Alcohol With One Mole of Ethylene Oxide

Designation	Moles of EO [Value A]	Area % [Value B]	EO Contribution [Value (A) (B)]
NO EO	0	54.8	0.000
EO 1	1	19.6	0.196
EO 2	2	10.2	0.204
EO 3	3	6.8	0.204
EO 4	4	5.5	0.220
EO 5	5	2.1	0.105
EO 6	6	0.7	0.042
EO 7	7	0.2	0.014
EO 8	8	0.1	0.008
	Total	100.0%	
	Total calculated moles added		0.993

Unlike the kinetics observed with the ethoxylation of fatty alcohols, the base-catalyzed reaction of ethylene oxide with fatty acids is divided into two stages. The first is a stage in which negligible product forms. Slowly, the reaction of the acid and ethylene oxide begins after an induction period to give mostly ethylene glycol monoester. In the second stage, after the addition of about one mole, the reaction rate increases (8). Clearly, the existence of an induction period in the ethoxylation process indicates that the reaction is one of a fatty acid and ethylene oxide, rather than a fatty alcohol and ethylene oxide.

As seen in Figure 2, the ethoxylation of fatty alcohols will not occur to an appreciable extent without a catalyst. The catalyst can be either acidic or, more typically, alkaline. Alkaline catalysts generally produce fewer by-products.

One of the by-products that is made in the ethoxylation of fatty alcohols is polyethylene

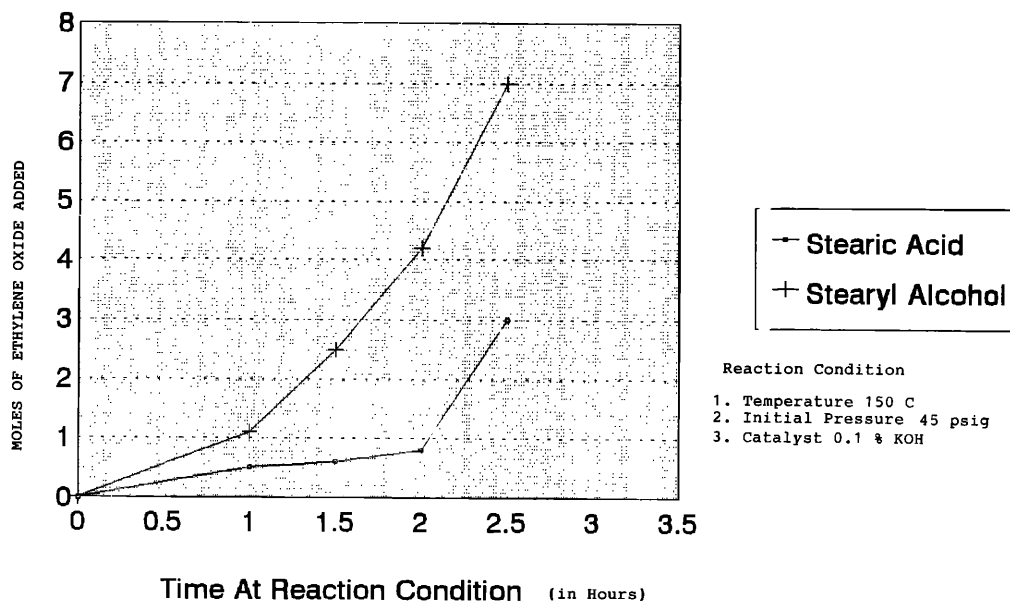


Figure 1. Moles of ethylene oxide added versus time.

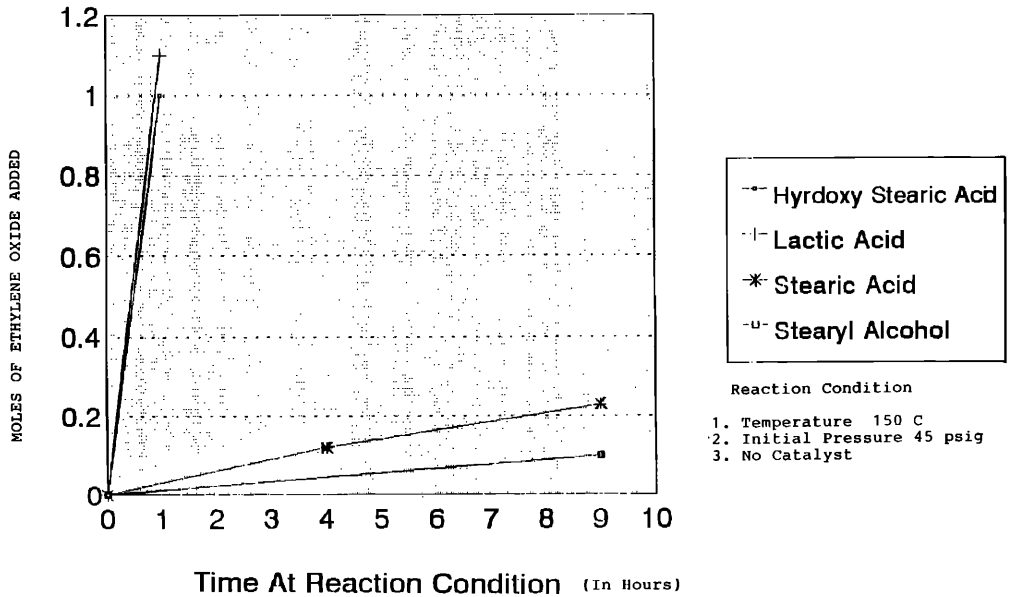


Figure 2. Ethoxylation rate (no catalyst).

glycol. This by-product concentration will be increased by having water present in the fatty material before ethoxylation.

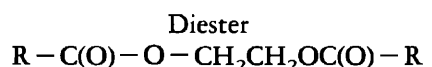
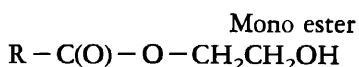
Published data (9,10) indicates that the concentrations of PEGs are as follows:

Hydrophobe	NaOH catalyst	Moles EO	Ethoxylate	PEG
Cetyl/stearyl alcohol	1.0	5.0	96.0%	4.0%
Lauryl alcohol	1.0	10.0	93.3%	6.7%
Lauryl alcohol	1.0	20.0	91.8%	8.2%
Lauryl alcohol	1.0	50.0	88.5%	11.5%

FATTY ACID ETHOXYLATION

Fatty acids when reacted with ethylene oxide produce complex mixtures of hydroxy esters. Unlike the products formed by the ethoxylation of fatty alcohols which are ethers, esters are formed when ethylene oxide is reacted with fatty acids. In addition to the oligomeric species that form during the reaction of a fatty acid with ethylene oxide, there is an added complication. That complication is the formation of diester.

ESTER PRODUCTS



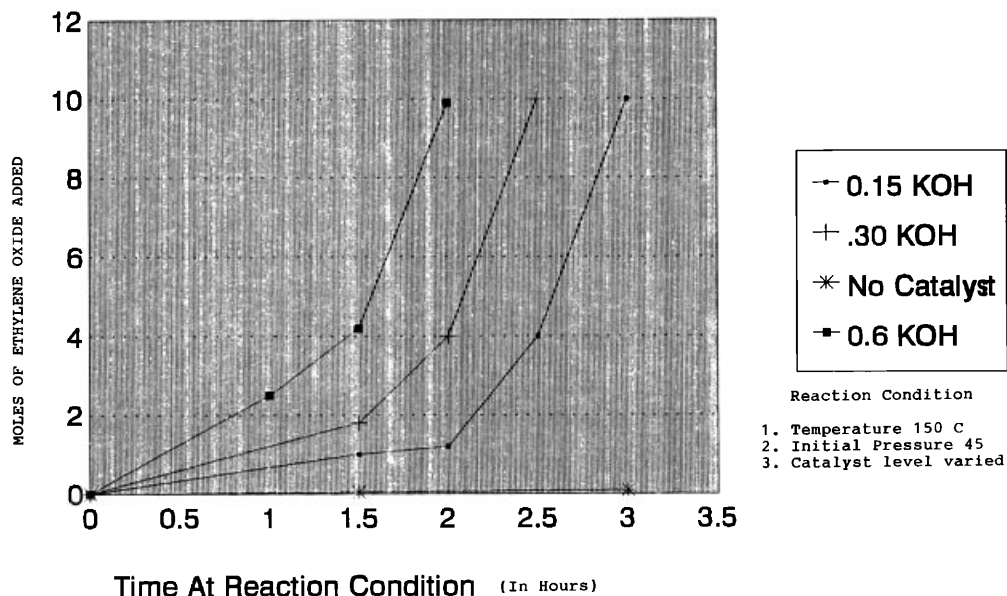


Figure 3. Stearic acid ethoxylation rates.

Published data indicate that the ratios of mono- to di- ester are as follows (11):

Hydrophobe	Moles EO	Mono ester	Diester	PEGS*
Stearic acid	9.0	38.9	41.1	20.0
Oleic acid	13.6	59.7	26.8	13.5

As earlier stated, the salient difference between fatty acid ethoxylation and fatty alcohol ethoxylation under base catalysis is that the former has an induction period. During this early stage of the reaction, there is a period of time in which there are negligible amounts of product formed. After that initial induction period, the reaction rate increases to about that of the fatty alcohol. As Figure 3 shows, increasing the amount of alkaline catalyst simply shortens the induction period but does not eliminate it.

The ethoxylation of fatty acids, like that of fatty alcohols, will not occur without a catalyst. The catalyst can be either acidic or, more typically, alkaline. Alkaline catalysts generally produce fewer by-products.

EXPERIMENTAL

HYDROGENATED CASTOR ETHOXYLATION—ETHENIFICATION REACTION

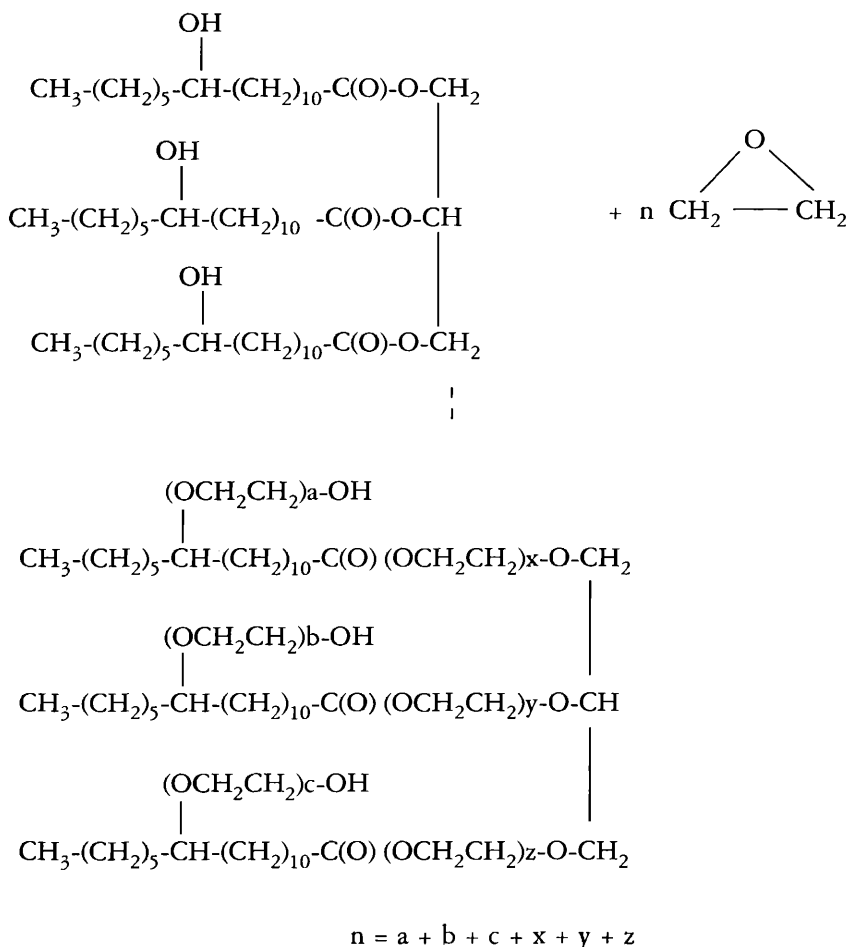
Hydrogenated castor oil is principally 12-hydroxystearic triglyceride. Hydrogenated castor ethoxylates are items of commerce and are commonly used in several applications, including textile and personal care applications. It was originally thought that these materials ethoxylated almost exclusively on the hydroxyl group. It is now under-

* PEGS are polyoxyethylene glycol.

stood that this material ethoxylates in an unusual manner. The process called ethenification is well known and is outlined in equation 1.

The ethylene oxide is added both to the ester group and to the hydroxyl group. It is therefore possible to evaluate the relative amounts of ethylene oxide that adds to each functionality. In short, there is a group selectivity or preference for ethoxylation. This group selectivity can be classified as strong, intermediate, or weak, depending on the results obtained with the ethoxylation.

Equation 1 (idealized)



The material to be ethoxylated is introduced into a clean dry vessel with the desired catalyst, if any. When all the ethylene oxide has been added, the molar ration of ethylene oxide to fatty material is one to one. The contents are then heated to 150°C under agitation. Vacuum is applied to 20 mm for one hour, to remove any water. The vacuum is released, and ethylene oxide is applied under pressure. The contents are then ethoxylated at 150°C and 45 psig. After all the oxide has been added, the reaction mass is held for one hour at 150°C.

Our analysis of the above reaction using one mole of ethylene oxide with one mole equivalent of hydrogenated castor oil, using 0.1% KOH as catalyst, gave the following results:

Ester reaction	58%
Hydroxyl group	29%
Polyethylene glycol	13%

12-HYDROXYSTEARIC ACID ETHOXYLATION

12-hydroxystearic acid is prepared by the saponification and purification of hydrogenated castor oil. Bullen (12) studied the ethoxylation of 12-hydroxystearic acid using base catalyst. His conclusions were that "it appears that the condensation product of ethylene oxide with 12-hydroxystearic acid is not affected by the type of catalyst used in its preparation and the polyethenoxy-12-hydroxystearate so obtained by using KOH, under base catalysis all the oxide was added to the carboxyl group" (6).

Our base catalyzed ethoxylation of 12-hydroxystearic acid resulted in the confirmation of the Bullen results:

Catalyst	Initial acid value	Final acid value	Rxn time (hr)	Final OH value	% Diester
0.2 KOH	164.2	0.5	1.5	247.2	25.1
0.1 KOH	164.2	0.1	1.1	244.1	24.0

The ethoxylation of one mole of hydroxystearic acid with one mole of ethylene oxide using 0.1% KOH as a catalyst resulted in 99% of the ethylene oxide reacting at the carboxyl group, with essentially no reaction at the hydroxyl group and about 1% polyethylene glycol. The major surprise, based upon the observations of Bullen, was that the induction period normally anticipated with the ethoxylation of a fatty acid was totally absent. The rate of ethoxylation was almost identical to that of a fatty alcohol, and very dissimilar to that of a fatty acid. The distribution of products and the group selectivity were as anticipated by Bullen.

As a control, one mole equivalent of stearic acid was ethoxylated with one mole equivalent of ethylene oxide:

Catalyst	Initial acid value	Final acid value	Rxn time (hr)	Final OH value	% Diester
0.2 KOH	172.2	4.06	1.25	137.3	19.9

These results matched well with the results of Wrigley (7).

CATALYSTS

Realizing that neither fatty alcohols nor fatty acids ethoxylate without a catalyst, we tried to ethoxylate 12-hydroxystearic acid without a catalyst. To our surprise, the material ethoxylated without an induction period. The rate was comparable to the rate of ethoxylation of the base-catalyzed fatty alcohol ethoxylation.

The product types that resulted after the ethoxylation of one mole equivalent of 12-

hydroxystearic acid with one mole of ethylene oxide and no catalyst were very similar to those of the ethoxylation of castor oil with a catalyst:

Catalyst	Initial acid value	Final acid value	Rxn time (hr)
No KOH	164.2	69.2	1.5
Determined by			
Carboxyl ethoxylation		57.8	Acid value
Hydroxyl ethoxylation		29.0	C13 NMR
PEGs		13.2	Extract

ETHOXYLATION OF BLENDS

In an attempt to determine if there was some catalytic effect of having both a hydroxyl and carboxyl group present in the reaction mass, we attempted to ethoxylate a blend of octadecanol and stearic acid. As anticipated, no reaction occurred without a catalyst. When no catalyst was added to the blend of octadecanol and stearic acid, the reaction rate for the blend was essentially zero. When 0.1% KOH catalyst was added to the blend of octadecanol and stearic acid, the reaction rate for the blend approximated the average of the rates of each component.

These results would indicate that the mere presence of both the carboxyl and hydroxyl group in the solution was not the reason for the ethoxylation of 12-hydroxystearic acid without a catalyst. We speculated that both functionalities need to be present in the same molecule and perhaps in a specific location. The question was partly addressed by the ethoxylation of lactic acid.

ETHOXYLATION OF LACTIC ACID

We investigated the ethoxylation of lactic acid without a catalyst. Lactic acid is beta hydroxy propionic acid.

We found that the ethoxylation does in fact occur without a catalyst and has the same kinetics as the ethoxylation of hydroxystearic acid. However, lactic acid ethoxylation without a catalyst occurs almost exclusively at the carboxyl group:

Catalyst	Initial acid value	Final acid value	Rxn time (hr)
No KOH	623.4	7.0	1.5
Determined by			
Carboxyl ethoxylation		98.8	Acid value
Hydroxyl ethoxylation		0.1	C13 NMR
PEGs		1.1	Extract

While the ethoxylation of lactic acid could not answer the question of the importance of the relative position of the groups to each other, because we now only have two data points, the data does clearly show that (a) the catalyst-free ethoxylation is not limited

to 12-hydroxystearic acid and (b) the group selectivity of the ethoxylation reaction of lactic acid differs considerably from the group selectivity of ethoxylation of 12-hydroxystearic acid.

ETHOXYLATION RATES

Table III outlines the amount of ethylene oxide added to various hydroxy-containing compounds. It shows that stearic acid, because of the anticipated induction period, ethoxylates significantly more slowly than the alcohols evaluated. Stearyl alcohol, castor oil, and 12-hydroxystearic acid all exhibit about the same rate of ethoxylation. Nonylphenol, which has a more acidic hydroxyl group than a primary or secondary alcohol, ethoxylates most rapidly.

Table III shows the amount of ethylene oxide added to various hydrophobes using 0.1% KOH catalyst. Stearyl alcohol has added 4.2 moles of ethylene oxide in two hours, while nonylphenol has added 9.5 moles in the same time.

CONCLUSIONS

We have found that the ethoxylation of 12-hydroxystearic acid and lactic acid are unusual in several respects:

1. Unlike typical fatty acids or alcohols, 12-hydroxystearic acid and lactic acid both ethoxylate without a catalyst. This could be explained by the presence of both a hydroxyl and a carboxyl in the reaction solution or the presence of both groups in the same molecule. The attempt to ethoxylate a blend of fatty acid and fatty alcohol without a catalyst did not succeed. Consequently, it appears that the two groups need to be present in the same molecule. We suggest that some type of complex forms between the oxide and the carboxyl and hydroxyl groups. We would also predict that the location of the hydroxyl group relative to the carboxyl group is important, but we do not have the needed data to prove that at this time.
2. There is a high degree of group selectivity to the ethoxylation of 12-hydroxystearic acid and lactic acid. The carboxyl group ethoxylates almost exclusively under base catalyst. When no catalyst is used, 33% of the added oxide goes to the hydroxyl group and 67% to the carboxyl group when one mole of oxide is added to 12-hydroxystearic

Table III
Moles of Ethylene Oxide Added Versus Time at Reaction Conditions

Time (hrs)	0.1 KOH				
	Nonyl phenol	Stearyl alcohol	Castor oil	12-hydroxy stearic acid	Stearic acid
0	0	0	0	0	0
1.0	4.9	1.1	1.4	1.0	0.5
1.5	7.5	2.5	3.3	2.2	0.6
2.0	9.5	4.2	6.1	4.3	0.8
2.5	11.1	7.0	8.2	6.8	3.0

acid. The carboxyl group of lactic acid ethoxylates almost exclusively when it is ethoxylated with one mole of ethylene oxide without a catalyst.

3. Despite the fact that the carboxyl group of 12-hydroxystearic acid ethoxylates almost exclusively under base catalyst, and predominately with no catalyst, the reaction rate does not show an induction period, which would be expected for carboxyl group ethoxylation. This difference in kinetics would suggest another mechanism for the reaction under both conditions. Ethoxylation of lactic acid likewise shows no induction period.

4. The ethoxylation of both 12-hydroxystearic acid and lactic acid, which predominately occurs on the carboxyl group, follows reaction rates approximating that of primary alcohols under base catalyst, despite the fact that the hydroxyl groups in both acids are secondary hydroxyl groups.

5. The following is the relative order of reaction of various hydrophobes with one mole of ethylene oxide arranged from the fastest to the slowest:

Fastest ethoxylation

nonyl phenol
lactic acid
stearyl alcohol = castor oil = 12-hydroxystearic acid
stearic acid

Slowest Ethoxylation

ACKNOWLEDGMENT

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