Ethoxylation

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ABSTRACT

The translation of the potentially hazardous, highly exothermic alkoxylation reaction to the rapid, safe and completely reliable industrial technology that it is today has been a noteworthy development. Commercially, the reactions of ethylene oxide with fatty acids are conducted in the presence of alkaline catalysts at temperatures above 100 C. The reaction proceeds in two steps. The first step is relatively slow and the product is predominantly ethylene glycol monoester. The second step occurs after approximately one mole ethylene oxide is reacted and all of the fatty acid is consumed. An increase in the ethylene oxide addition rate is observed, and polyethylene glycol esters are formed. Rapid transesterification also occurs, and the molar proportions of monoester, diester, and free polyol in the product approaches those predicted by the equilibrium assuming random esterification of the polyethylene glycol hydroxyl groups. The composition of polyoxyethylated fatty acids is similar to that obtained by the direct esterification of fatty acid with polyethylene glycol. The distribution of the ethylene oxide chain lengths in the polyethylene glycol portion of the product can be approximated assuming random addition of the epoxide.

INTRODUCTION

The reaction of ethylene oxide with fatty acids is an important industrial method for manufacturing nonionic surfactants (1,2). This reaction and the use of polyethylene glycol stearates as emulsifying agents were first described in 1928 (3). The first detailed study of these products was made by Schöller. In 1930 Schöller demonstrated that hydrophobic substances such as fatty acids or alcohols become water soluble when they are combined with polyoxyethylene chains of sufficient length, and he studied the wetting and detergent properties of these products.

Surfactants can be classified in four general categories depending upon the charge of the active group in aqueous media: anionic (sodium dodecylbenzene sulfonate); cationic (cetyltrimethyl ammonium bromide); amphoteric (alkylbetaines); nonionic (fatty acid ethoxylates). The nonionics of which fatty acid ethoxylates are but one example are, as the name implies, electrically neutral. They are compatible with ionic surfactants and are frequently used as coemulsifiers.

A nonionic is an effective surfactant because it is composed of two parts, a hydrophobic, or water insoluble part, and a hydrophilic, or water soluble part. The fatty acid is the hydrophobic part, and its strength depends upon the number of methylene groups in the fatty acid chain. The oxyethylene chain is the hydrophilic part of the molecule. The hydrophilicity of the oxyethylene chain is attributed to the tendency of the ether oxygen to associate with water molecules through hydrogen bonding. This tendency is relatively weak, and a fairly large number of ethylene oxide links is required to solubilize a fatty acid. It has been estimated that about 1 ethylene oxide unit is required to solubilize each methylene unit. Thus, by varying the ratio of ethylene oxide to fatty acid in the molecule, products ranging from oil soluble to completely water soluble can be produced. The physical state of fatty acid ethoxylates also depends on the fatty acid and extent of oxyethylation. Polyoxyethylene esters of the higher fatty acids are solids at room temperature. The lower ethoxylates of unsaturated fatty acids are liquids, and solid products are obtained as the oxyethylene chain length is increased. Fatty acid ethoxylates are generally less soluble and have poorer foaming and wetting properties than their ethoxylated alcohol counterparts (4). They are also susceptible to hydrolysis in strongly acid or alkaline solutions yielding polyethylene glycols and fatty acid or fatty acid soap.

MANUFACTURE

Polyethylene glycol esters of fatty acids are produced industrially either by the reactions of ethylene oxide with fatty acid (Equation I) or by the esterification of fatty acid with polyethylene glycols (Equation II).

$$\mathrm{RCOOH} + n\mathrm{C_2H_4O} \rightarrow \mathrm{RCOO(C_2H_4O)_nH} \qquad \mathrm{I}$$

$$\mathrm{RCOOH} + \mathrm{HO(C_2H_4O)_nH} \rightarrow \mathrm{RCOO(C_2H_4O)_nH} + \mathrm{H_2O} \qquad \mathrm{II}$$

Both processes are conducted under conditions which cause ester interchange equilibrium and hence should produce similar products. Ultimately both processes depend upon ethylene oxide chemistry, since the polyethylene glycol used in the esterification reaction is produced by reacting ethylene oxide with ethylene glycol or lower polyethylene glycols. The reactions of ethylene oxide with either ethylene glycol or ethylene glycol esters are not very specific, and the product contains a mixture of polyethylene glycols of varying chain lengths. The average chain and the peak of the distribution curve corresponds to n, the moles of ethylene oxide reacted.

Ethylene oxide is a hazardous chemical and must be stored and handled with care. It is highly explosive in the presence of oxygen and has recently been classified as a suspected carcinogen. Ethylene oxide is a very reactive chemical, and its reactions are highly exothermic (ca. 20 kcal/g mole). It can polymerize explosively at elevated temperatures or in the presence of catalysts such as acids or bases. The safe and reproducible manufacture of ethylene oxide condensates requires explosion proof equipment with good temperature control and efficient agitation. The equipment must be thoroughly clean and dried to eliminate unwanted byproducts such as polyethylene glycols. The reaction is usually conducted in the presence of an inert gas such as nitrogen or methane. Adequate cooling must be provided to dissipate the heat of reaction. Ethylene oxide is added stepwise, and the conditions are controlled so that large amounts (>4%) of unreacted ethylene oxide do not accumulate in the reactor. Overcooling of the reactor should also be avoided since it may stop the reaction and permit excess ethylene oxide to accumulate. Fatty acid ethoxylations are usually conducted at temperatures of 110-180 C, preferably between 130-165 C. An alkaline catalyst is used at a level of ca. 1 to 3 mole % of the fatty acid charge. Sodium hydroxide, potassium hydroxide, sodium acetate and sodium oleate are typical examples of the catalysts used. The partial pressure of ethylene oxide in the reactor can be maintained at ca. 30 to 60 psig.

Most fatty acid ethoxylates are manufactured by a batch process using either a stirred reactor or a circulating reactor (5,6). Circulating reactors provide better mixing and better control, thus resulting in greater throughput and more uniform products. Agitated reactors, on the other hand, can handle more viscous products.

A diagram for a stirred reactor (7) is shown in Figure 1. The jacketed reaction kettle is made of stainless steel and is heated by introducing steam to the jacket. Cooling water is also provided to control the reaction temperature and to cool the finished product. The kettle is provided with a thermowell, a pressure gauge, a safety valve or rupture disc, a drain and lines for introducing ethylene oxide, nitrogen and vacuum. Check valves are also provided in the ethylene oxide addition lines so that the catalyst containing product cannot be sucked back into the ethylene oxide charge tank. Provisions are also made to automatically shut off the ethylene oxide supply if the reaction temperature or pressure rises above the limits for which the equipment was designed.

The fatty acid and catalyst are charged to the reactor and the system is evacuated and purged with nitrogen. The mixture is heated to the desired temperature and ethylene oxide is cautiously added. Once the reaction starts, heat is no longer applied to the vessel. The rate of ethylene oxide addition is controlled so that the cooling system can maintain the desired reaction temperature. After the ethylene oxide is added, the mixture is kept at reaction temperature until all of the residual ethylene oxide reacts. When no further pressure change is observed, the product is cooled. Final product processing may consist of catalyst neutralization, vacuum removal of ethylene oxide traces and filtration.

A circulation reactor (8) is shown in Figure 2. Fatty acid and catalyst are charged to the feed tank A and the mixture is heated and dried. The mixture is transferred by the pump B and the line F into the top of the reactor D through the spray nozzle G. Liquid ethylene oxide under nitrogen pressure from the feed tank E is also introduced into the top of the reactor D where it immediately vaporizes and comes into contact with the atomized feed. The entire charge is circulated from the bottom of the reactor through the line F or the heat exchanger C and back into the top of the reactor. The temperature of the reactor is maintained by the controller H which activates the valve J which directs part or all of the circulating feed through the heat exchanger C. The entire reaction takes place under a nitrogen atmosphere. The ethylene oxide pressure is monitored by the controller I which regulates the flow of ethylene oxide to the reactor through the valve K. The reaction mixture is continuously circulated during the ethylene oxide addition and afterwards until all of the absorbed epoxide is reacted.

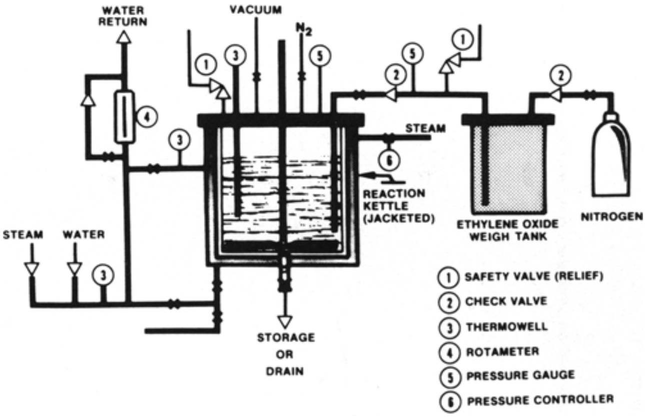


FIG. 1. Ethylene oxide batch reactor.

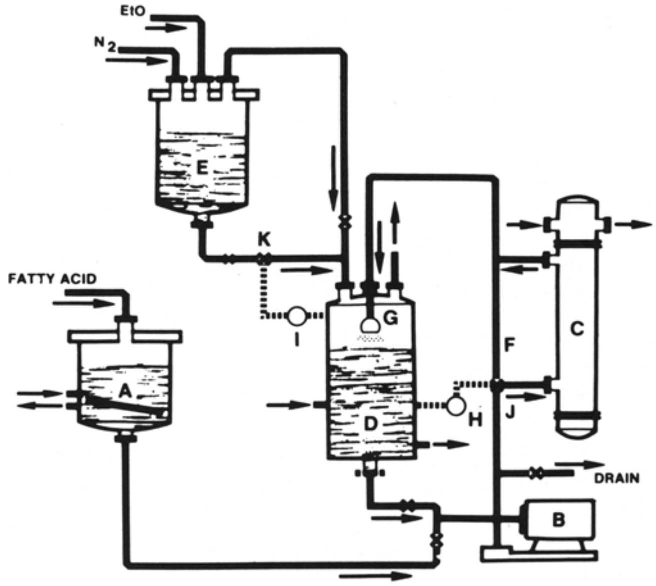


FIG. 2. Ethylene oxide circulation reactor.

CHEMISTRY

Fatty Acid Ethoxylation

The alkaline catalyzed reaction of ethylene oxide with fatty acid occurs in two steps (9,10) represented by Equations III and IV.

$$RCOOH + C_2H_4O \rightarrow RCOOC_2H_4OH \qquad III$$

$$RCOOC_2H_4OH + (n-1)C_2H_4O \rightarrow RCOO(C_2H_4O)_nH \qquad IV$$

The initial step is the reaction of ethylene oxide with the fatty acid to produce ethylene glycol monoester. The second step is the reaction of ethylene oxide with the glycol monoester to produce polyethylene glycol esters. Ester interchange can also occur under alkaline conditions, and the product is a mixture of monoester, diester, and free polyol.

$$2\ RCOO(C_2H_4O)_nH \rightleftharpoons RCOO(C_2H_4O)_n\ OCR + HO(C_2H_4O)_nH \qquad V$$

The initial reaction of ethylene oxide with fatty acid is relatively slow (Fig. 3) and lasts until ca. 1.1 moles ethylene oxide per mole fatty acid are reacted. It is followed by a much faster ethylene oxide uptake which continues for the duration of the reaction.

The variation of product composition with ethylene oxide chain length is shown in Figure 4. The initial reaction is fairly specific resulting in a linear decrease in fatty acid accompanied by a linear increase in the concentration of ethylene glycol monoester. Ethylene oxide chain growth is obviously slow since the fatty acid is completely consumed when ca. 1.1 moles of ethylene oxide per mole acid are reacted. The monoester concentration at this point reaches a maximum mole fraction of ca. 0.75. Ester interchange or transesterification occurs slowly, and small but significant amounts of diester and free polyol are produced.

The point at which the free fatty acid vanishes coincides with the kinetic change observed in Figure 3. This point is also accompanied by an abrupt change in product composition. The concentration of monoester decreases and the concentrations of free polyol and diester increase. Further addition of ethylene oxide results in minor variations in the relative amounts of free polyol, monoester and diester. These changes are probably caused by variations in the solubility of the free polyol in the reaction mixture. After several moles of ethylene oxide per mole fatty acid are reacted, the product contains free polyol, monoester and diester in the mole ratios of 1.15:2.00:1.00. If all of the

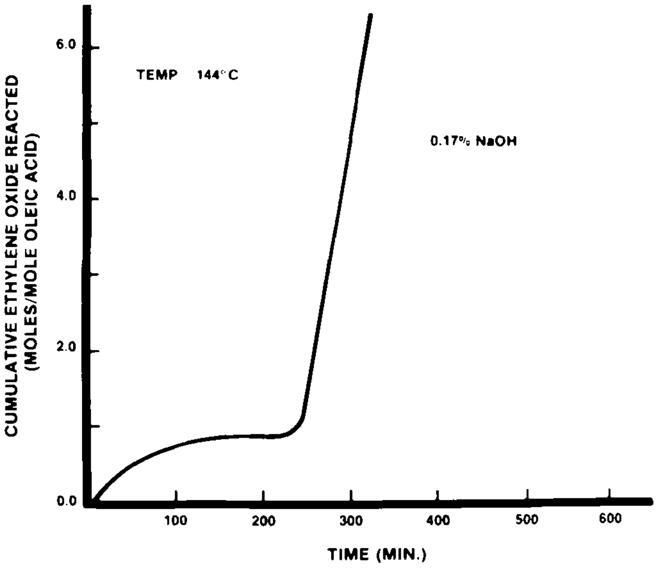


FIG. 3. Consumption of ethylene oxide by reaction with oleic acid.

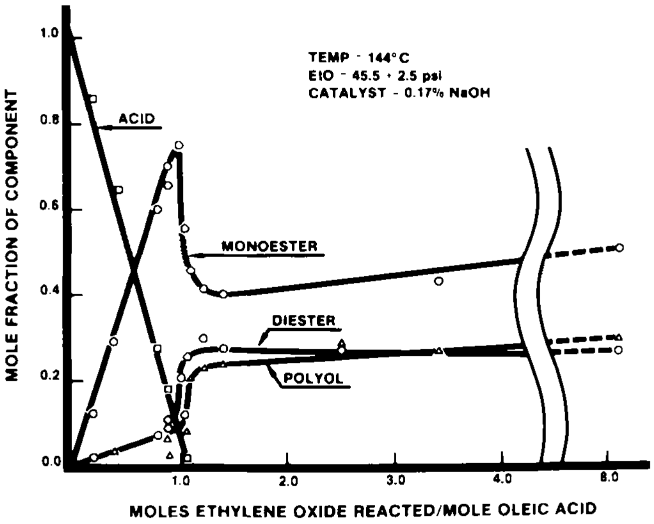


FIG. 4. Variation of product composition with moles of ethylene oxide reacted with oleic acid.

competing hydroxyl groups in the ester interchange reaction 5 were equally reactive, one would predict free polyol, monoester, and diester mole ratios of 1.0:2.0:1.0, and the constant for the equilibrium equation VI will be 4 (11).

$$K = (\text{Monoester})^2/(\text{Polyol})\ (\text{Diester}) = 4 \qquad \text{VI}$$

The observed values are in reasonable agreement. The slight excess of polyol can be attributed to the catalyst which introduces water and hence ultimately glycol into the reaction mixture.

$$NaOH + RCOOH \rightarrow RCOONa + H_2O \qquad \text{VII}$$

$$HOH + C_2H_4O \rightarrow HOC_2H_4OH \qquad \text{VIII}$$

Ethylene oxide chain growth is slow in the first stage of the reaction. As mentioned, the average ethylene oxide chain length in this step is constant at about 1.15. After all of the fatty acid is reacted, chain growth occurs more or less randomly on the available hydroxyl groups. Ester interchange is also rapid in the second stage of the reaction, and both free and combined polyols grow at about the same rate. Chain growth as shown here for the monoester occurs in a series of successive competitive reactions.

$$RCOOC_2H_4OH + C_2H_4O \rightarrow RCOO(C_2H_4O)_2H \qquad \text{IX}$$

$$RCOO(C_2H_4O)_2H + C_2H_4O \rightarrow RCOO(C_2H_4O)_3H \qquad \text{X}$$

$$RCOO(C_2H_4O)_{n-1}H + C_2H_4O \rightarrow RCOO(C_2H_4O)_nH \qquad \text{XI}$$

Each step produces higher polyethylene glycol esters which can compete for ethylene oxide with ethylene glycol monoester or each other. If the relative rates of these competitive steps are equal, the distribution of ethylene oxide chain lengths in the polyol will approximate a Poisson distribution (12). The mole fraction X of each component containing n ethylene oxide units can be calculated by Equation XII.

$$X_x = e^{-V}V^{n-1}/(n-1)! \qquad \text{XII}$$

where V is the moles of ethylene oxide reacted per mole ethylene glycol. The polyol distribution obtained in the reaction of ethylene oxide with stearic acid was shown to approximate a Poisson distribution (13).

Mechanism of Fatty Acid Ethoxylation

The variations in reaction rate and product composition observed during the ethoxylation of fatty acids can be explained by the simplified mechanism shown in Table I. The initial reaction occurs through the carboxylate ion which is formed from the catalyst according to Equation III and reacts with ethylene oxide according to Equation XIV. The product is a strongly basic alkoxide ion which is immediately neutralized with fatty acid to produce ethylene glycol monoester and regenerate the carboxylate ion as shown in Equation XV. This reaction is fast and irreversible and limits the formation of polyethylene glycol esters. Equations XIV and XV represent the predominant reactions which occur during the first step. They account for the almost stochiometric reaction of the fatty acid and the predominance of monoester in the product. The formation of diester and free polyol either by reactions XVI and XVII or by the ester interchange reaction XIX is slow.

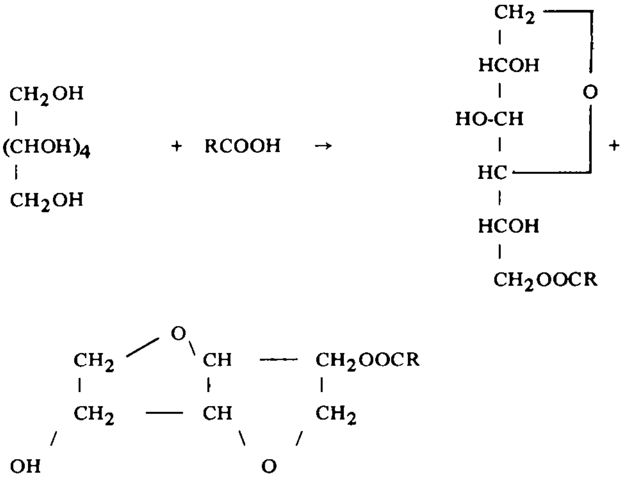
Once all of the fatty acid is consumed, reaction XV can no longer occur and the concentration of the alkoxide ions increases. The strongly basic alkoxide ion is an excellent catalyst for polyoxyethylation, and chain growth XVIII can occur. It also catalyzes the rapid ester interchange reaction XIX. Thus, the concentrations of the polyol, monoester, and diester approach the equilibrium values, and both free and combined polyol increase in oxyethylene chain length at about the same rate.

Fatty Acid Ester Ethoxylation

The oxyethylation of fatty acid ester is also used industrially in the manufacture of surfactants. The most important members of this group are the anhydro sorbitol esters which are produced by reacting fatty acids with sorbitol. This reaction is accompanied by anhydrization of the sorbitol, and the product is a mixture of anhydro sorbitol esters of which 1,4-sorbitan and isosorbide are two of the principal components (Equation XX). The reaction is conducted under conditions which promote ester interchange, and the fatty acid is distributed among the various available hydroxyl groups.

TABLE I

$RCOOH$	$+ {}^{-}OH$	$\xrightarrow[\text{fast}]{\text{very}}$	$RCOO^-$	+ HOH	XIII
$RCOO^-$	$+ C_2H_4O$	$\xrightarrow[\text{slow}]{}$	$RCOOC_2H_4O^-$		XIV
$RCOOC_2H_4O^-$	+ RCOOH	$\xrightarrow[\text{fast}]{\text{very}}$	$RCOOC_2H_4OH$	$+ RCOO^-$	XV
$RCOOC_2H_4OH$	$+ RCOO^-$	→	$RCOOC_2H_4OOCR$	$+ {}^{-}OH$	XVI
$-OH$	$+ C_2H_4O$	→	$HOC_2H_4O^-$		XVII
$RCOO(C_2H_4O)_{x-1}^-$	$+ C_2H_4O$	→	$RCOO(C_2H_4O)_x^-$		XVIII
$RCOO(C_2H_4O)_x^-$	$+ RCOO(C_2H_4O)_yH$	⇌	$RCOO(C_2H_4O)_xOCR$	$+ HO(C_2H_4O)^-_y$	XIX



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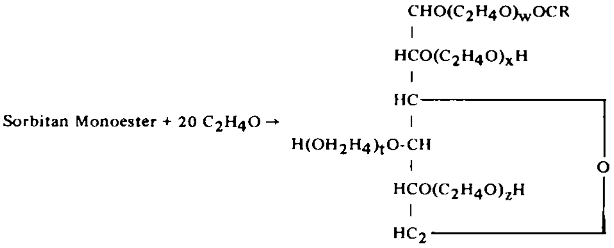
The oxyethylation reaction is conducted under basic conditions which also promotes ester interchange resulting in more or less random addition of ethylene oxide to the hydroxyl groups. Thus, a 20 mole ethoxylate, known commercially as polysorbate 20, can be pictured as a sorbitan monoester with 4 ethylene oxide chains of varying length. The total chain length (w + x + y + x) averages 20 units per molecule. The fatty acid will not only be distributed along these chains, but some ethoxylated sorbitan molecules will also contain 0 or 2 or more fatty acids per molecule. The same type of ethylene oxide chain length and fatty acid distribution will be expected for the other anhydro sorbitol moieties in the product.



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REFERENCES

1. Schönfeldt, N., "Surface Active Ethylene Oxide Adducts," Pergamon Press, 1969.
2. Schick, M.J., "Nonionic Surfactants," Marcel Dekker, 1967.
3. French Patent 664,261.
4. Wrigley, A.N., F.D. Smith, and A.J. Stirton, JAOCS 34:39 (1957).
5. Malkemus, J.D., JAOCS 33:571 (1956).
6. Davidsohn, A., and B.M. Milwidsky, "Synthetic Detergents," 6th Edition, p. 144, John Wiley and Sons, New York, 1978.
7. Ethylene Oxide Technical Bulletin, Jefferson Chemical Company, 1956.
8. Wilson, R.A., U.S. Patent 2,586,769.
9. Stockburger, G.J., and J.D. Brandner, JAOCS 43:6 (1966).
10. Wrigley, A.N., F.D. Smith, and J.D. Stirton, Ibid. 36:34 (1959).
11. Satkowski, W.B., S.K. Huang, and R.L. Liss, "Nonionic Surfactants, Edited by M.J. Schick, Chapter 5, Marcel Dekker, 1967.
12. Flory, P.J., JAOCS 62:1561 (1940).
13. Birkmeier, R.L., and J.D. Brandner, J. Agric. Food Chem. 6:471 (1958).

Tall Oil Fatty Acids

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ABSTRACT

About 1949, with the advent of effective fractional distillation, the tall oil industry came of age, and tall oil fatty acids (TOFA), generally any product containing 90% or more fatty acids and 10% or less of rosin, have grown in annual volume ever since, until they amount to 398.8 million pounds annual production in the U.S. in 1978. Crude tall oil is a byproduct of the Kraft process for producing wood pulp from pine wood. Crude tall oil is about 50% fatty acids and 40% rosin acids, the remainder unsaps and residues; actually, a national average recovery of about 1-2% of tall oil is obtained from wood. On a pulp basis, each ton of pulp affords 140-220 pounds black liquor soaps, which yields 70-110 pounds crude tall oil, yielding 30-50 pounds of TOFA. Separative and upgrading technology involves: (a) recovery of the tall oil; (b) acid refining; (c) fractionation of tall oil; and occasionally (d) conversion to derivatives. TOFA of good quality and color of Gardner 2 corresponds to