Synthetic Detergents from Animal Fats. VIII. The Ethenoxylation of Fatty Acids and Alcohols[1, 2]

A. N. WRIGLEY, F. D. SMITH, and A. J. STIRTON, Eastern Regional Research Laboratory,[3] Philadelphia, Pennsylvania

THE NONIONIC SURFACE-ACTIVE AGENTS, a comparatively new development in this country, are inherently versatile and have excellent growth potential (9). The most important are made by the reaction of ethylene oxide with alkyl phenols, tall oil, fatty acids or alcohols, amides, amines, or mercaptans. As the first part of a research program on the utilization of animal fats, in this case as nonionic surface-active agents and detergents, it seemed appropriate to carry out a laboratory survey of the reaction of ethylene oxide with individual fatty acids and alcohols, particularly those derivable from animal fats.

Accordingly the reaction of ethylene oxide in the presence of an alkaline catalyst with a series of purified acids and alcohols was interrupted at selected stages to obtain nonionic surface-active agents, covering a range of about 9 to 50 in the average number of ethenoxy groups per molecule. The acids used were lauric, myristic, palmitic, stearic, oleic, monohydroxystearic, 9,10-dihydroxystearic, phenylstearic, and o-xylylstearic; and the alcohols were dodecanol, tetradecanol, hexadecanol, octadecanol, m-xylyloctadecanol, and oleyl.

The purified saturated acids and alcohols were prepared from good commercial grades by vacuum distillation and low-temperature crystallization methods. Purified oleic acid and oleyl alcohol were prepared by published methods (6, 18). Monohydroxystearic acid, m.p. 69–70°, from the sulfation of oleic acid, was a mixture of several position isomers (10). 9,10-Dihydroxystearic acid, from the oxidation of elaidic acid, was the high-melting form, m.p. 127.5–128° (17). Phenylstearic acid, o-xylylstearic acid, and m-xylyloctadecanol were prepared by the Friedel and Crafts reaction (15).

Reaction with Ethylene Oxide

The reaction with ethylene oxide was carried out as shown in Figure 1, following essentially the procedures of Karabinos and co-workers (1, 5), using a magnetic stirrer instead of a gas dispersion tube. The catalyst was 0.5% K_2CO_3 for the fatty acids, and 0.5% KOH for the alcohols. The charge of catalyst and acid or alcohol was heated under nitrogen atmosphere to the reaction temperature, usually 185°. The gentle flow of nitrogen was then halted, the bubbling tubes containing mineral oil were adjusted to the positions shown in the figure, and the nitrogen was replaced by ethylene oxide, initiating vigorous agitation at the same time. After half an hour the stopcock on the center neck was closed, and the supply of ethylene oxide was thereafter kept in harmony with the rate of reaction; a small excess was lost at the left-hand bubbler. The reaction was followed by increase in weight. Samples of 20 g. or more were withdrawn at stages such that n, the average number of ethenoxy groups per molecule, had values of about 10, 15, 20, 30, and 40. The value of n used was actually based on the saponification equivalent in the case of acids, and on weight in the case of alcohols. Data obtained relating refractive index and the number of ethenoxy groups were a useful guide in later experiments.

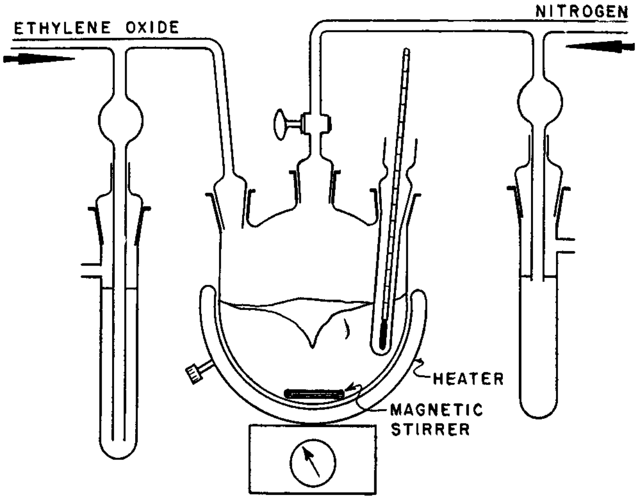


FIG. 1. Apparatus for the reaction of ethylene oxide with

At room temperature most of the products were pale yellow plastic solids. Liquids or semi-solids were generally obtained in the ethenoxylation of arylstearic, hydroxystearic, and dihydroxystearic acids and at low values for n (10 or 15) in the ethenoxylation of lauric, myristic and oleic acids, and dodecanol.

Experience with the laboratory preparation of ethenoxylated acids and alcohols suggested a convenient method for comparing reaction rates. This led to consideration of reaction mechanism.

Mechanism and Reaction Rate

The rates of the reaction of ethylene oxide with stearic acid and octadecanol, using 0.5% KOH, were compared at a constant temperature of 160° and at identical flow rates of ethylene oxide (5 l./hr.). For this purpose a graduated 50-ml. centrifuge tube[4] was modified at the bottom to introduce ethylene oxide and at the top for connection to a flow meter. The entering ethylene oxide bubbles provided satisfactory agitation. Constant flow was maintained by a T-tube adjustably immersed in mineral oil, and constant temperature by a thermostated oil bath. With a charge of about 15-ml. initial volume at 160°

---

[1] Presented at the meeting of the American Oil Chemists' Society, Chicago, September 24–26, 1956.

[2] For number VII in this series see reference 14.

[3] A laboratory of the Eastern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

[4] Pyrex Cat. No. 8100 illustrates the type. Reference to a particular manufacturer does not imply recommendation by the U. S. Department of Agriculture over other manufacturers not mentioned.

it was convenient to follow the reaction by increase in volume, refractive index, and in the case of stearic acid by (A) fall in acid number and (B) increase in saponification equivalent. These data were related to the number of moles of ethylene oxide combined, as shown in Figure 2.

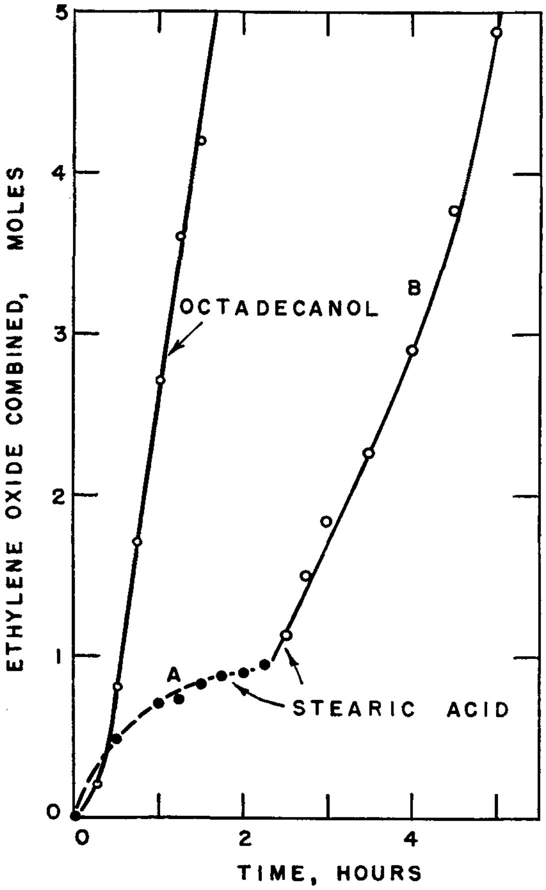


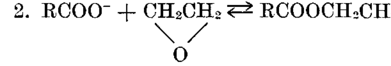
FIG. 2. Reaction rate, ethenoxylation of stearic acid and octadecanol.

The reaction of octadecanol with ethylene oxide was rapid, in harmony with attack by the strongly basic alcoholate ion. The straight-line relation, apparently resulting from approximately constant mole fraction concentrations of alcoholate ion and ethylene oxide, indicates a zero order rate constant of 3.6 moles per hour. The essentially equal acidity of all product ether alcohols, $R(OC_2H_4)_nOH$, should make their reaction with ethylene oxide random (8, 19). The parent alcohol may however be somewhat less acidic and less reactive than the ether alcohols (19).

Reaction of ethylene oxide with stearic acid (Figure 2) shows marked inflection and a low rate of reaction at the junction of segments A and B, corresponding to the formation of ethylene glycol monostearate. The data of segment A plotted on a logarithmic scale gave a straight line, indicating, with the mole fraction of stearate ion and ethylene oxide essentially constant, that the first stage of the reaction is first order in stearic acid, with a rate constant of 1.15 reciprocal hours. Segment B seems to approach the plot for octadecanol in shape and slope.

The first-order dependence of reaction rate on stearic acid concentration requires that the free carboxylic acid be assigned a definite role in the mechanism. With this in mind equations similar to those of previous discussions (1, 13) are appropriate:

1. $OH^- + RCOOH \rightarrow \overset{\uparrow}{H_2O} + RCOO^-$

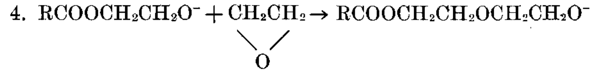


2. $RCOO^- + \underset{\diagdown O \diagup}{CH_2CH_2} \rightleftarrows RCOOCH_2CH_2O^-$

3. $RCOOCH_2CH_2O^- + RCOOH \rightarrow RCOOCH_2CH_2OH + RCOO^-$

The effectiveness of the attack on ethylene oxide in Equation 2 would be somewhat reduced by the low base strength of the carboxylate ion. The equilibrium however is displaced in the desired direction with the help of the free acid of Equation 3; the carboxylate catalyst is regenerated. The acidity of the carboxyl group would thus assure virtually complete conversion of the acid to ethylene glycol monostearate before further ethenoxylation occurs.

As removal of the acid proceeds, Reaction 3 slows down. When no more acid is available, the strongly basic alcoholate ion takes over the function of catalyst, and the reaction becomes rapid and non-selective, as with octadecanol:



4. $RCOOCH_2CH_2O^- + \underset{\diagdown O \diagup}{CH_2CH_2} \rightarrow RCOOCH_2CH_2OCH_2CH_2O^-$

The ethenoxylation of fatty acids may be further complicated by the formation of a certain amount of by-product, polyethylene glycols and their diesters, ascribed to transesterification reactions (7).

Ethenoxylation of monohydroxystearic acid and 9,10-dihydroxystearic acid, from evidence presented in the case of 12-hydroxystearic acid (1), presumably occurs only at the carboxyl group.

Surface-Active and Related Properties

The surface-active and related properties of the ethenoxylated fatty acids and alcohols, including solubility, cloud point, surface and interfacial tension, detergency, wetting, foaming, and emulsification were measured, without removal of the small amount of alkaline catalyst.

Solubility

Ethenoxylated alcohols were more soluble than ethenoxylated acids. At room temperature, with an average of about 10 ethenoxy groups per molecule, 0.25% solutions of ethenoxylated dodecanol, tetradecanol, oleyl alcohol, and monohydroxystearic acid were clear and transparent. Under the same conditions, solutions of ethenoxylated lauric, myristic, oleic, and dihydroxystearic acids were slightly turbid; and ethenoxylated palmitic, stearic, phenylstearic, and xylylstearic acids gave somewhat more turbid solutions.

Cloud Point

The cloud point, a measure of the inverse solubility characteristic of nonionic surface-active agents, was determined by gradually heating 1% solutions in a controlled temperature bath and recording the temperature at which clear or nearly clear solutions became definitely turbid. The reproducibility of this temperature was checked by cooling the solutions until they became clear again. The ethenoxylated alcohols showed sharp and reproducible cloud-points. The cloud points of the ethenoxylated acids were less sharp and not easily reproduced on cooling. In some cases observations were easier with 0.5% solutions.

Ethenoxylated alcohols gave cloud points only at n = 10. The cloud points were 88, 75, 74, 68, and 57° for ethenoxylated dodecanol, tetradecanol, hexadecanol, octadecanol, and oleyl alcohol, respectively. The cloud point thus decreased with increasing molecular weight of the saturated alcohol. At n = 15 and greater the solutions remained clear even at 100°.

The cloud point for 1% solutions of ethenoxylated acids was measured at various values of n, from about 9 to 45. Curves were drawn, from which the values of Table I were obtained. In contrast to the ethenoxylated alcohols the cloud point for ethenoxylated saturated acids generally increased with the molecular weight of the acid. The hydroxy and arylstearic acids generally had the lowest cloud-points.

TABLE I

Cloud Point, °C., of 1% Solutions of Ethenoxylated Acids

Acids	Ave. No. of Ethenoxy Groups Cloud Points °C.					
	10	15	20	25	30	35
Lauric	46	70	79	83	85	87
Myristic	....	65	80	86	89	92
Palmitic	54	70	85	....	>100	....
Stearic	....	75[a]	92	94	>100	....
Oleic	....	82[a]	85	87	89	92
Hydroxystearic	....	39	67	87	91	93
9,10-Dihydroxystearic	32[a]	47	62	72	78	83
Phenylstearic	....	49	65	78	89	....
o-Xylylstearic	....	....	63	75	82	87

[a] 0.5% solutions.

Surface and Interfacial Tension

Surface and interfacial tensions of 0.1% solutions were measured with the Du Noüy tensiometer at room temperature (28°). The range of values for ethenoxylated saturated fatty acids and alcohols is shown in Figures 3 and 4 together with the curves for ethenoxylated oleic acid and oleyl alcohol. With respect to the ranges shown, generally higher values were obtained with the higher molecular weight acids and alcohols. Surface-tension values were generally higher for ethenoxylated alcohols; for example at n = 15, 20, and 30 the values were 36.4, 38.2, and 40.2 dynes/cm. for ethenoxylated hexadecanol, and 34.2, 35.8, and 38.4, respectively, for ethenoxylated palmitic acid. As shown by Figure 3, in many cases minimal interfacial-tension values for ethenoxylated acids were obtained between about n = 15 and 18. Ethenoxylated lauric, myristic, palmitic, and oleic acids had minimum values in this region.

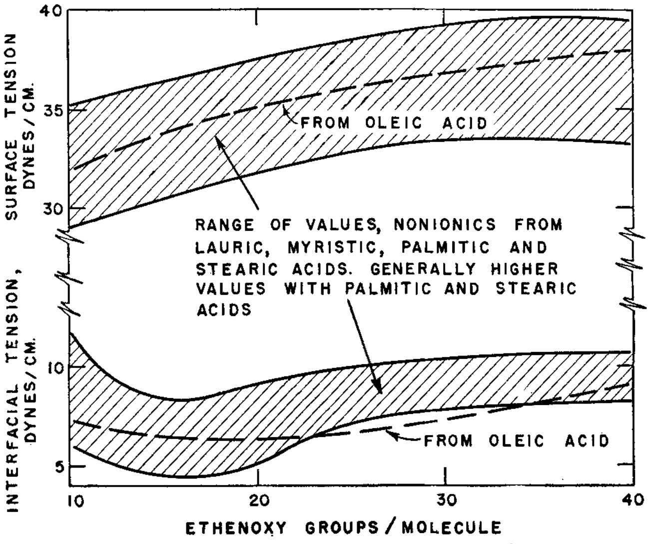


Fig. 3. Surface and interfacial tension of 0.1% solutions of ethenoxylated acids.

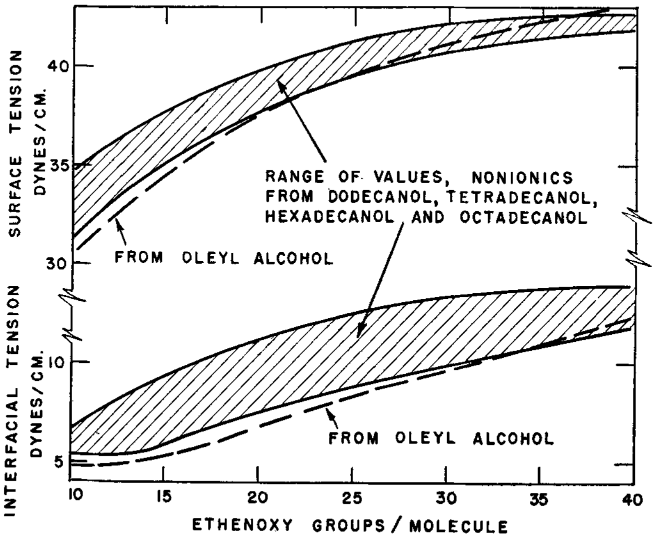


Fig. 4. Surface and interfacial tension of 0.1% solutions of ethenoxylated alcohols.

Detergency

Detergency was measured as the increase in reflectance, △R, after washing 10 swatches of A.C.H. No. 114[5] standard soiled cotton in the Terg-O-Tometer[5] for 20 min. at 120°F. and at 110 cycles per minute. Table II records the detergency of built solutions of ethenoxylated acids and alcohols, at an average of approximately 10 and 20 ethenoxy groups per molecule. The built solutions (Table II, footnotes) were better detergents than corresponding unbuilt 0.25% solutions, and the builder alone was able to remove considerable soil. By analysis of variance (4) a dif-

TABLE II

Detergency of Built Solutions[a] of Ethenoxylated Fatty Acids and Alcohols; 0.25% Solutions in Hard Water of 300 p.p.m. (Terg-O-Tometer, 20 min. at 120°F., 110 cycles/min., 10 swatches A.C.H. No. 114/l.)

	Detergency, △R[b]	
	n = 10	n = 20
Nonionic Detergents from Acids		
Lauric	35.6	36.9
Palmitic	......	36.8
Stearic	36.6	36.9
Oleic	37.8	36.4
Hydroxystearic	......	38.2
Dihydroxystearic	......	38.3
Phenylstearic	......	37.8
Xylylstearic	......	38.6
Nonionic Detergents from Alcohols		
Dodecanol	36.2	36.9
Tetradecanol	......	36.9
Octadecanol	......	36.1
Oleyl alcohol	......	36.7

[a] The built solutions were 0.05% with respect to the ethenoxylated acid or alcohol and 0.20% with respect to the builder. The builder was 25% $Na_4P_2O_7$, 25% $Na_5P_3O_{10}$, 48.75% Na_2CO_3, 1.25% CMC (16). The △R value for 0.20% builder, alone, was 28.7.

[b] △R = Increase in reflectance after washing. For comparison the values for unbuilt 0.25% sodium dodecyl sulfate and 0.25% ethenoxylated stearic acid (n = 16) were 25.9 and 26.9, respectively.

---

[5] Reference of a commercial product does not imply recommendation by the U. S. Department of Agriculture over other commercial products not mentioned.

ference in ΔR of 1.0 was significant with 95% probability.

Most of the built detergents were equally effective. Of the 16 values, 10 were in the range 36.1–36.9. The best detergents were ethenoxylated aryl- and hydroxystearic acids ($n = 20$) and ethenoxylated oleic acid ($n = 10$). The data of Table II and other similar experiments not tabulated do not indicate significant differences among the ethenoxylated 12, 14, 16, and 18 carbon-saturated acids and alcohols. The conditions of measurement did not disclose optimum values for n, except that ethenoxylated lauric acid was a better detergent at $n = 20$ and ethenoxylated oleic acid at $n = 10$.

Wetting Properties

The wetting properties of 0.1% solutions in hard water (300 p.p.m.) were measured at 25°, using standard binding tape, a 1-g. hook, and 40-g. anchor (12). Curves were drawn from data at several values of n, from which the wetting times in seconds, at $n = 10$ and 20, were as follows:

	$n=10$	$n=20$
Lauric acid	30	38
Myristic acid	38	60
Palmitic acid	160	85
Stearic acid	380	125
Oleic acid	100	76
Dihydroxystearic acid	53	56
Phenylstearic acid	530	200
Dodecanol	16	58
Tetradecanol	18	50
Hexadecanol	30	52
Octadecanol	100	105
Oleyl alcohol	30	50

Ethenoxylated alcohols were better wetting agents than the acids. The presence of a double bond or of hydroxyl groups improved wetting properties.

A maximum in wetting properties (minimum in sinking time) was shown in several cases, as illustrated in Figure 5. This seemed to occur at about $n = 10$, 14, 15, 15, and 20 for nonionic wetting agents from oleyl alcohol, oleic acid, octadecanol, stearic acid, and phenylstearic acid, respectively. Ethenoxylated palmitic and dihydroxystearic acids also had optimum wetting properties in the same range.

Foaming Properties

The foam height of 0.25% solutions in hard water (300 p.p.m.) was measured by the Ross-Miles pour test (11) at 60°. Foam was unstable in all cases. The immediate foam height of ethenoxylated acids was generally about 20 to 50 mm. at $n = 15$ and about 50–80 mm. at $n = 30$. The ethenoxylated alcohols (Figure 6) had higher immediate foam and showed maxima at about $n = 17$ to 19.

Emulsifying Properties

Emulsions were prepared by intermittent violent shaking (2). A stoppered, 500-ml. Erlenmeyer flask containing 40 ml. of light petrolatum and 40 ml. of an aqueous solution 0.1% with respect to the emulsifying agent, was manually shaken in 5 cycles. Each cycle consisted of 5 violent downward motions and 1 minute of standing. The emulsion was then poured into a 100-ml. graduate, and the time required for 10 ml. of the aqueous phase to separate was recorded.

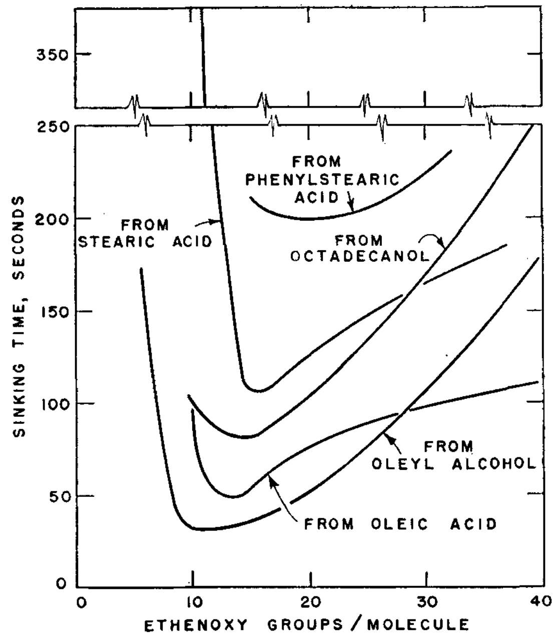


FIG. 5. Wetting properties of ethenoxylated fatty acids and alcohols; 0.1% solutions in hard water (300 p.p.m.).

The ethylene oxide type of nonionic, surface-active agents appeared to have excellent general emulsifying properties according to this test. Ethenoxylated 12, 14, 16, and 18 carbon-saturated and unsaturated acids and alcohols, containing from 15 to 30 ethenoxy groups, gave values of the same magnitude, the average being about 1,500 seconds (25 min.). Ethenoxylated hydroxy- and arylstearic acids were also good emulsifying agents but less efficient in this test, with an average of about 800 seconds. For comparison the value for sodium oleate and for several anionic surface-active agents was less than 200 seconds.

Esterification of Polyethylene Glycols

The ester type nonionic surface-active agents may also be prepared by esterification. In the case of 9,10-

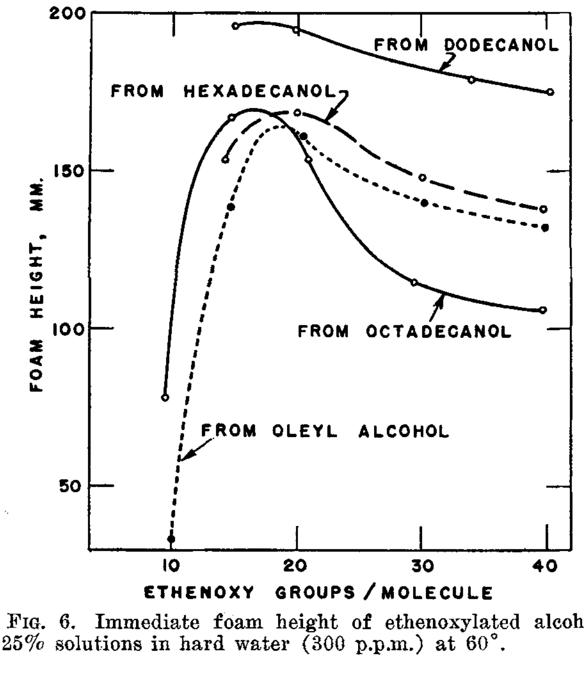


FIG. 6. Immediate foam height of ethenoxylated alcohols; 0.25% solutions in hard water (300 p.p.m.) at 60°.

dichlorostearic acid [m.p. 45-45.6°, from the low temperature additive chlorination of elaidic acid (20)] ethenoxylation was unsuccessful, perhaps because acidic by-products destroyed the alkaline catalyst. Accordingly 9,10-dichlorostearic acid was esterified with an equimolar ratio of a commercial polyethylene glycol, having an average of about 14 ethenoxy groups, in the presence of 0.1% naphthalene-β-sulfonic acid catalyst, in 24 hrs. at 125°. The product was a yellow liquid. Analysis for iodine number (zero), acid number (0.43), and percentage of chlorine (7.38) suggested almost complete conversion to $CH_3(CH_2)_7CHClCHCl(CH_2)_7CO_2(C_2H_4O)_{14}H$. Actually, however, a certain amount of polyethylene glycol and diester is to be expected. This chlorinated nonionic surface-active agent had solubility, wetting, foaming, and emulsifying properties similar to ethenoxylated oleic acid. The surface and interfacial tension values of a 0.1% solution at 28° were 33.8 and 6.0 dynes/cm., respectively.

Summary

A laboratory survey of the properties of a series of ethenoxylated fatty acids and alcohols containing about 10, 15, 20, 30, and 40 ethenoxy groups per molecule has brought together information on solubility, cloud point, surface and interfacial tension, detergency, and wetting, foaming and emulsifying properties.

Ethenoxylated alcohols were generally more soluble and had better wetting and foaming properties than the acids. Ethenoxylated acids had generally lower surface and interfacial tension values. Both types of nonionics appeared to be excellent emulsifying agents. Most of the ethenoxylated acids and alcohols were equally effective as built detergents. Built ethenoxylated oleic acid (n = 10) and built hydroxy-, dihydroxy-, phenyl-, and xylylstearic acids (n = 20) were the best detergents.

Nonionic surface-active agents derivable from animal fats appeared to have an optimum range in the average number of ethenoxy groups per molecule, with respect to certain properties. The optimum was in the range of about 14 to 18 for wetting properties, the foaming properties of ethenoxylated alcohols, and the interfacial tension of ethenoxylated acids. This range is about equal to the value suggested for adequate solubility [3 less than the number of carbon atoms in the parent alcohol (3)] but somewhat higher than the general rule for maximum detergency [2/3 the number of carbon atoms in the parent acid or alcohol (1, 5)].

The rate of the reaction of octadecanol and stearic acid with ethylene oxide was compared. The alcohol reacted faster, in a non-specific manner. The acidity of the carboxyl group of stearic acid promoted conversion to ethylene glycol monostearate before further ethenoxylation occurred. After disappearance of the carboxylic acid the rate of the reaction of the ethenoxylated acid approached that for octadecanol. A reaction mechanism consistent with these results is proposed.

Acknowledgment

Surface and interfacial tension measurements were made by E. W. Maurer. This assistance is acknowledged with thanks.

REFERENCES

1. Ballun, A. T., Schumacher, J. N., Kapella, G. E., and Karabinos, J. V., J. Am. Oil Chemists' Soc., *31*, 20–23 (1954).
2. Briggs, T. R., J. Phys. Chem., *24*, 120–6 (1920); Martin, A. R., and Hermann, R. N., Trans. Faraday Soc., *37*, 25–9 (1941).
3. Cohen, M., Compt. rend., *226*, 1366–8 (1948).
4. Duncan, D. B., "Multiple Range and Multiple F Tests," Virginia Agricultural Experiment Station, Technical Report No. 6 (1953).
5. Karabinos, J. V., Bartels, G. E., and Kapella, G. E., J. Am. Oil Chemists' Soc., *31*, 419–20 (1954).
6. Knight, H. B., Jordan, E. F. Jr., Roe, E. T., and Swern, Daniel, "Biochemical Preparations," *2*, 100–4, John Wiley and Sons Inc. (1952).
7. Malkemus, J. D., J. Am. Oil Chemists' Soc., *33*, 571–4 (1956).
8. Patat, F., Cremer, E., and Bobleter, O., J. Polymer Science, *12*, 489–96 (1954). (Discussion, by A. J. Lowe and B. Weibull, 493–6).
9. Rainey J. L., and Denoon, C. E. Jr., Chem. Eng. News, *31*, 4521–3 (1953).
10. Roe, E. T., Schaeffer, B. B., Dixon, J. A., and Ault, W. C., J. Am. Oil Chemists' Soc., *24*, 45–8 (1947).
11. Ross, J., and Miles, G D., Oil and Soap, *18*, 99–102 (1941).
12. Shapiro, L., Am. Dyestuff Reptr., *39*. 38–45, 62 (1950).
13. Shechter, L., and Wynstra, J., Ind. Eng. Chem., *48*, 86–93 (1956).
14. Stirton, A. J., Maurer, E. W., and Weil, J. K., J. Am. Oil Chemists' Soc., *33*, 290–1 (1956).
15. Stirton, A. J., Schaeffer, B. B., Stawitzke, Anna A., Weil, J. K., and Ault, W. C., J. Am. Oil Chemists' Soc., *25*, 365–8 (1948).
16. Stoltz, E. M., Ballun, A. T., Ferlin, H. J., and Karabinos, J. V., J. Am. Oil Chemists' Soc., *30*, 271–3 (1953).
17. Swern, D., Billen, G. N., Findley, T. W., and Scanlan, J. T., J. Am. Chem. Soc., *67*, 1786–9 (1945).
18. Swern, D., Knight, H. B., and Findley, T. W., Oil and Soap, *21*, 133–9 (1944).
19. Weibull, B., and Nycander, B., Acta Chem. Scand., *8*, 847–58 (1954).
20. Weil, J. K., Stirton, A. J., and Maurer, E. W., J. Am. Oil Chemists' Soc., *32*, 148–51 (1955).

[Received September 19, 1956]

A Note on Improved Isolation of Concentrates of Linolenic Acid and Ethyl Linolenate from Linseed Oil[1]

WINFRED E. PARKER and DANIEL SWERN, Eastern Regional Research Laboratory,[2]
Philadelphia, Pennsylvania

The isolation of concentrates of linolenic acid from linseed oil (1, 2, 3, 4, 6) or perilla oil (6) by urea complex separation methods has been described. Although 87% concentrates can be obtained in good yield from perilla oil, its limited availability makes it a poor choice of starting material for large-scale laboratory work. Linseed oil, on the other hand, is plentiful, but poor yields, low purity (70% or less), or a combination of the two, are obtained from it when published procedures are used.

The need developed in our laboratory for kilogram quantities of linolenic acid and ethyl linolenate of 80% or higher purity. This note describes the procedures used in their preparation in good yield from linseed oil fatty acids or ethyl esters. The success of the procedures depends upon the use of sufficient urea to blend with at least 50% of the linseed oil fatty acids or esters at room temperature. Lower temperatures (0–4°C.), as reported in the literature,

---

[1] This note is IV in the series, "Application of Urea Complexes in the Purification of Fatty Acids, Esters, and Alcohols." Paper III is reference 6.

[2] A laboratory of the Eastern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.