



Fig. 1. Apparatus for oxyethylation under constant pressure, temperature, and stirring rate, with measured level of liquid ethylene oxide.

in isopropyl alcohol solution, this solvent was removed by vacuum evaporation.

Removal of Parent Diol. In the case of products containing sufficient surviving parent glycol to interfere seriously with water solubility, this residual diol was destroyed by oxidation. A major part of the *meso*-diol could be removed first by crystallization.

For example, *meso*-9,10-octadecanediol oxyethylated to $n = 4.00$ was found to contain 20.30% unreacted octadecanediol. By crystallization of the product mixture (31 g.) from ether at 0° and then at -20° , 5.50 g. of *meso*-octadecanediol, out of 6.29 g. expected, was removed. The remaining product in 175 ml. of ether was shaken repeatedly with 4.0 g. (7 equivalents/equivalent) of periodic acid in 250 ml. of water, with which it formed an emulsion. After 1.3 hr., 100 ml. of a saturated solution of potassium iodide were added; the iodine was immediately reduced with thio-sulfate solution. After boiling off the ether and heating the mixture to 60° , the aqueous layer was saturated with sodium sulfate and separated. After three more washings at 60° with saturated solutions of sodium sulfate the organic layer was freed from non-aldehyde by distillation at 0.05 mm., leaving an oxyethylated product devoid of parent diol.

Oxyethylation of *threo*-9,10-Dihydroxystearonitrile.
Preparation of Nonionic Soaps. The possibility that oxyethylation would involve the nitrile group was shown to be minor by a preliminary experiment in which equimolar amounts of *dl*-9,10-octadecanediol and stearonitrile were treated with 6 moles of ethylene oxide; 96.3% of the stearonitrile was recovered unchanged.

threo-9,10-Dihydroxystearonitrile was accordingly caused to react with 4-, 6-, and 8-molar proportions of ethylene oxide under the same conditions used for the octadecanediols. The resulting oxyethylated nitriles were converted to nonionic soaps by refluxing in aqueous alcohol with excess alkali, conversion to a solution of the carboxylic acid by ion exchange, exact neutralization to pH 9, and rotary evaporation of solvent.

Reaction Rates

The oxyethylation apparatus was convenient for kinetic measurements, which were made in the course of several preparations. In such cases the stirring rate was controlled at 1,900 rpm by operating the magnetic stirrer through a voltage stabilizer and variable transformer; speed was checked several times by a stroboscopic tachometer (5). Typical results in the

oxyethylation of *meso*- and *dl*-9,10-octadecanediol and *threo*-9,10-dihydroxystearonitrile with respective rates 7.7, 8.3, and 10.9×10^{-5} moles/sec., are shown in Fig. 2. Aside from slight initial curvature these compounds gave straight-line plots of ethylene oxide (ml. or moles) vs. time, as reported for *n*-octadecanol (17). This was to be expected under conditions of constant ethylene oxide pressure and constant molar concentrations of catalyst and hydroxy groups.

Consumption of Parent Diol

Weibull and Nycander (13) showed that the distribution of products in the oxyethylation of water, methanol, ethanol, ethylene glycol, and ethoxyethanol is described by the equations:

$$v = c \ln n_{oo}/n_o - (c-1) (1 - n_o/n_{oo})$$

$$n_i/n_{oo} = c^{i-1}/(c-1)! \left\{ n_o/n_{oo} - (n_o/n_{oo})^c \sum_{j=0}^{i-1} 1/j! \left[(c-1)! \ln n_{oo}/n_o \right]^j \right\}$$

in which

- N_i = molecule with i added ethylene oxide molecules
- m = number of moles of ethylene oxide consumed
- n_{oo} = number of moles of starting compound
- n_o = number of moles of surviving starting compound
- n_i = number of moles of N_i in reaction product
- k_i = velocity constant for reaction of N_i with ethylene oxide
- k_o = velocity constant for reaction of starting compound with ethylene oxide
- $c = k_i/k_o$ = distribution constant
- $v = m/n_{oo}$ = average number of moles of ethylene oxide per mole of starting compound

The base-catalyzed oxyethylation of long-chain primary alcohols (20) obeys the Weibull-Nycander equations with distribution constants c of about 3.

The amount of parent octadecanediol remaining at various degrees of oxyethylation was determined by the periodate method (10) and recorded in Table I. It is seen that, at comparable degrees of oxyethylation, less *dl* than *meso*-diol survives in each case. Although the amounts of various individual oxyethylated products were not determined, the quantity of residual glycol was used in the first equation to calculate an approximate distribution constant. Thus for *meso*-9,10-octadecanediol a distribution constant of 6 to 8 is suggested; for the *dl*-diol, about 3.

Distillation of a reaction product of 90.64 g. of *dl*-octadecanediol and 3.0 moles per mole of ethylene oxide (n , or $v = 3$) was undertaken to obtain further data on the distribution of products. With a spinning

TABLE I
Surviving Starting Glycol

Substance oxyethylated	Degree of oxyethylation, n , or v	Surviving starting glycol, %	Distribution constant, ^a $c = k_i/k_o$
9,10-Octadecanediol			
<i>meso</i>	4.00	20.30	7.5
<i>dl</i>	4.00	10.48	3.3
<i>meso</i>	7.87	6.40	6.4
<i>dl</i>	8.09	1.78	3.2
<i>meso</i>	12.12	2.14	6.0
<i>dl</i>	11.86	0.39	3.1
<i>meso</i>	16.26	1.44	7.5
<i>dl</i>	16.01	< 0.1
9,10-Dihydroxystearonitrile			
<i>threo</i>	4.03	5.90	2.2
<i>threo</i>	8.03	1.40	2.8

^a Calculated from $v = c \ln n_{oo}/n_o - (c-1) (1 - n_o/n_{oo})$.

TABLE II
Surface-Active Properties

Surface-active agent	Average number of oxyethyl groups, n	Cloud point, 1%	Wetting time, ^a 0.1%, sec.	Surface and interfacial tension, 0.1% dynes/cm.		Foam height (8), immediate, 0.25%, 60°, mm.	Emulsion stability, ^b 2% in light petrolatum	Detergency ^c 60°, 300 ppm ΔR	
				S.T.	I.T.			0.25%	0.05% +0.2% builder
Oxyethylated 9,10-octadecanediols									
meso.....	4 ^d ^e	25.0	26.0	1.6	15	4 days
dl.....	4 ^d ^e	87.0	26.0	1.9	7	2 days
meso.....	8 ^d ^e	17.0	26.6	1.7	40	1500 sec.
dl.....	8 ^d ^e	23.0	26.9	2.2	40	510 sec.
meso.....	12 ^d	51.5°	6.1	26.9	2.1	100	140 sec.
dl.....	12	48.5°	6.3	27.5	2.4	105	190 sec.	12	27
meso.....	16	83.0°	14.0	28.7	3.5	100	70 sec.
dl.....	16	83.0°	15.0	30.1	4.1	125	80 sec.	13	26
Oxyethylated <i>threo</i> -9,10-dihydroxystearonitriles.....	4 ^e	19.0	31.4	5.0	0	200 sec.	8	27
	6 ^e	14.0	34.8	7.4	0	200 sec.	8	28
	8	34.2°	8.8	33.1	3.7	2	100 sec.	8	26
Nonionic soaps.....	4 ^f	29.0	31.4	5.0	65	90 sec.	15	26
	8 ^f	300.0	33.1	3.7	30	80 sec.	14	26
Oxyethylated									
oleic acid.....	15	82.0°	49.0	33.2	6.5	30	1200 sec.	14	26
stearic acid.....	15	79.0°	106.0	34.4	6.5	2	1200 sec.	14	23
oleyl alcohol.....	10	57.0°	30.0	30.4	4.7	40	1750 sec.	14	24
octadecanol.....	10	68.0°	103.0	34.5	6.8	50	2100 sec.	16	23

^a Shapiro standard tape method (9). ^b Atlab emulsion tester, time for 10% separation from emulsion of 25 ml. 2% solution in mineral oil with 25 ml. water. ^c Launder-Ometer, A.C.H. standard soiled cotton. ΔR = increase in reflectance after washing = 16 and 25, respectively, for Na dodecyl sulfate. Builder = 25% Na₄P₂O₇, 25%, Na₅P₃O₁₀, 48.75% Na₂CO₃, 1.25% CMC (11). ^d Purified by removal of unreacted diol. ^e Too turbid for cloud-point determination. ^f No cloud point below 100°.

solution. All compounds were quite soluble at n = 12 and n = 16.

Cloud point, wetting time, surface and interfacial tension, foam height, emulsion stability, and detergency values are recorded in Table II and compared with values for related nonionic surface-active agents.

Wetting time was measured by the Shapiro standard binding tape method (9). Optimum wetting properties were observed at n = 12 for the oxyethylated octadecanediols. The oxyethylated dihydroxystearonitrile may have optimum wetting properties at n = 8; in contrast, the corresponding nonionic soap has no wetting properties. The oxyethylated diols have the lowest surface and interfacial tension values at low values of n (n = 4) and greatest foam height at high values (n = 16). The foam is not permanent and falls rapidly.

Emulsifying properties were measured with the Atlab emulsion tester. Emulsions made from a 2% solution of the surface-active agent in 25 ml. of mineral oil (U.S.P. light petrolatum) and 25 ml. of water were shaken for 3 min., and the time required for 10% of the emulsion to separate as the aqueous phase was recorded. Oxyethylated 9,10-octadecanediol with 4 oxyethyl groups was found to have exceptional emulsifying properties under these conditions. A spontaneous emulsion formed on pouring the 2% solution into water. Aqueous solutions did not form stable emulsions.

Detergency was measured in the Launder-Ometer at 60° in hard water of 300 ppm, using A.C.H. standard soiled cotton. Built solutions, 0.05% with respect to the surface-active agent and 0.20% with respect to the builder [25% Na₄P₂O₇, 25% Na₅P₃O₁₀, 48.75% Na₂CO₃, 1.25% CMC (11)], were better detergents than unbuilt 0.25% solutions. With the exception of the oxyethylated dihydroxystearonitriles, which did not form clear solutions at 0.25% concentration in hard water at 60°, detergency was about equal to that for the other nonionic detergents listed, and equal to that for sodium dodecyl sulfate, the values for which were 16 and 25.

The nonionic soaps (n = 4, n = 8) had the salt-forming characteristics of soap but in other respects appeared to have typical nonionic characteristics. Calcium stability values (15) were greater than 1,800.

TABLE III
Metal Ion Stability of Nonionic Soaps^a
C₈H₁₇CH[(OC₂H₄)_xOH]CH[(OC₂H₄)_yOH](CH₂)₇CO₂Na

Number of oxyethyl groups, x+y=n	Metal Ion Stability								
	Mg ⁺⁺	Al ⁺⁺⁺	Ca ⁺⁺	Fe ⁺⁺	Ni ⁺⁺	Cu ⁺⁺	Zn ⁺⁺	Ba ⁺⁺	Pb ⁺⁺
4	100	10	100 ^b	5	100 ^b	6	14	100 ^b	15
8	100	100 ^c	100	11	100 ^d	11	100 ^e	100	100 ^f

^a Metallic ion stability = 10 x no. of ml. of 1% metal salt solution tolerated by 10 ml. of 1% surface-active agent (3).

^{b,c,d,e,f} Cloud points 27°, 34°, 45°, 52°, 50°, respectively.

Metal ion stability values (3) for the nonionic soaps are recorded in Table III. Increase in the number of oxyethyl groups markedly improved the stability to Al⁺⁺⁺, Zn⁺⁺, and Pb⁺⁺. On heating the test solution of the metal soap above room temperature, the listed cloud points were observed.

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