New Nonionic Detergents Derived from Epoxidized Oils. IV.[1]

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Abstract

The results of an experiment designed to investigate optimal composition, catalyst level, molar ratio, and cosolvent level for the reaction of methylepoxystearate with polyoxyethylene glycol are presented. These results show that nonionic wetting agents of possible technical value can be produced from methylepoxystearate and commercially available polyoxyethylene glycols. The reaction is catalyzed at ambient temperatures by the presence of about 0.25% boron trifluoride as its dihydrate in the absence of any coupling solvents. The reaction goes at ambient temperatures with the use of only the most rudimentary equipment and is relatively insensitive to formulation errors.

This makes it possible for small formulators to custom-produce their own nonionic surface-active agents and produce products with tailor-made properties. Since some of the systems initially are emulsions if no coupling cosolvent is present, care should be taken to insure that the raw materials are dry and the mixing is adequate. Companies with more sophisticated equipment can, of course, take advantage of the remaining functionality at the hydroxyl group and at the methyl ester end of the fatty chain, as has previously been described (2).

Introduction

Prior work (1–3) has indicated that potentially useful nonionic wetting agents can be derived from the reaction of epoxidized fatty esters and polyoxyethylene glycol. The polyoxyethylene glycol should have its molecular weight in the 300–2,000 range normally associated with satisfactory performance in other nonionic detergents. Most of this prior work has involved the use of cosolvents to achieve unified solutions during the reaction. Little work has been done to investigate the over-all effect of molar ratio, catalyst level, and other variables on the technical function of these materials.

It is the purpose of the present work to establish the feasibility of a simple procedure for manufacturing economically useful, nonionic surface-active agents from polyoxyethylene glycols and epoxidized fatty esters as depicted in Fig. 1. In addition, it is intended to demonstrate the formation of chemically stable, non-ionic surface-active agents in the most rudimentary processing equipment.

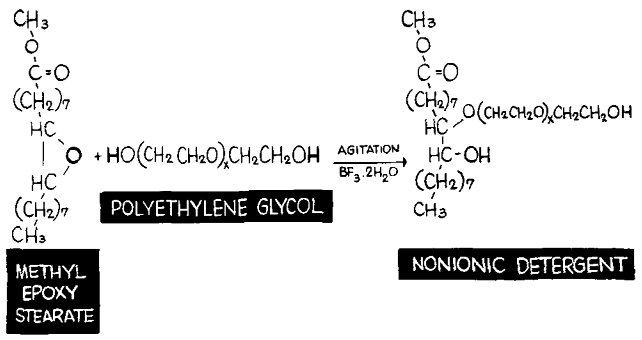

FIG. 1. Reaction studied.

Experimental Design

A complete replicate of a 2 × 2 × 2 × 3 factorial experiment was set up to investigate the main and interactive effects associated with variations in catalyst level, molar ratio of reactions, cosolvent level, and molecular weight of the polyoxyethylene glycol. The catalyst levels were set at 0.15% and 0.30% boron trifluoride dihydrate. The molar ratio was varied between a 10% deficiency and a 10% excess of the polyoxyethylene glycol which was required for mono addition. Benzene was used as a cosolvent at the 30% level in half of the reactions, but no cosolvent was used in the other half. The tests were carried out with polyoxyethylene glycols which had molecular weights of 300, 400, and 600.

The appropriate polyoxyethylene glycol, catalyst at the proper level, and benzene (where applicable) were combined in an 8-oz. flint glass jar, agitated by means of a magnetic stirrer. Methylepoxystearate was weighed into a beaker, then added at ambient temperature, while the balance of the ingredients were being agitated. Batch size was held constant at 200g. Those samples containing the benzene cosolvent were recovered by vacuum-stripping the benzene from the solution by using a rotary exaporator for a one-hour period at 80C. Ten milliliters of distilled water were added, and the process of evaporation was continued for an additional hour. The evaporation of the water removed the last traces of benzene as an azeotrope, as previously described (1).

TABLE I

Analysis of Variance

Source of variation	Degrees of freedom	Hydroxyl value Sums of squares	Hydroxyl value Mean square	Oxirane oxygen Sums of squares	Oxirane oxygen Mean square
Total	23	20411.998333		0.019169	
Treatment	23	20411.998333	887.478188	0.019169	0.000833
Molar ratio	1	689.081666	689.081666[a]	0.000308	0.000308
Catalyst level	1	141.135000	141.135000[a]	0.002521	0.002521
Benzene cosolvent	1	58.906666	58.906666[a]	0.006868	0.006868[a]
Type of Polyglycol	2	19112.960833	9556.480416[a]	0.002451	0.001225[a]
Ratio × catalyst interaction	1	25.214999	25.214999	0.000037	0.000037
Ratio × benzene interaction	1	42.666666	42.666666[a]	0.000280	0.000280
Ratio × polyglycol interaction	2	189.150833	94.575416[a]	0.000776	0.000388
Catalyst × benzene interaction	1	.806666	.806666	0.001504	0.001504[a]
Catalyst × polyglycol	2	3.607500	1.803750	0.000351	0.000175
Benzene × polyglycol interaction	2	40.175833	20.087916	0.001161	0.000580
Residual (3 factor and higher)	9	108.291666	12.032407	0.002910	0.000323

[a] Significant at .10 probability.

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[1] Presented at the AOCS meeting, May 1967, New Orleans, La.

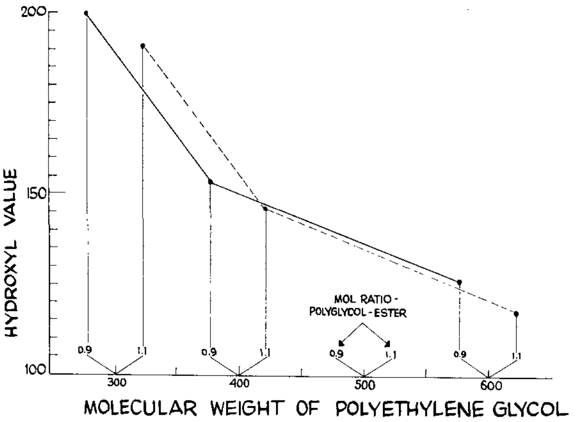

FIG. 2. Hydroxyl value as a function of mol ratio and polyethylene glycol molecular weight.

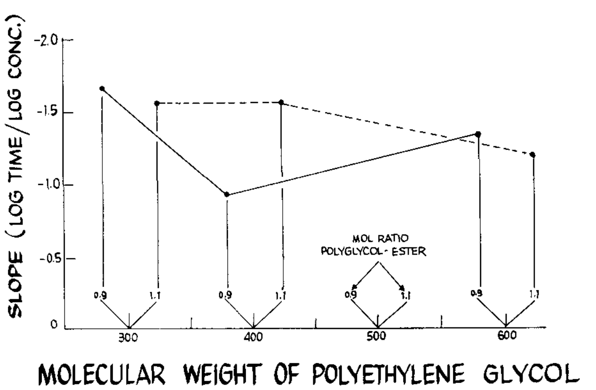

FIG. 4. Log-log slope of sinking time vs. concentration as a function of polyethylene glycol molecular weight.

Methods and Materials

Polyoxyethylene glycols with molecular weights of 300, 400, and 600 were obtained from the Dow Chemical Company. Boron trifluoride dihydrate, obtained from the General Chemical Division of the Allied Chemical Corporation, was used as the catalyst; the benzene was ACS reagent grade. The methylepoxystearate was prepared by the Development Division, Swift & Company, Chemicals for Industry Department, Hammond, Ind.

Sinking times were determined in accordance with the American Association of Textile Chemists and Colorists (4). Hydroxyl values were determined in accordance with the American Oil Chemists' Society (5). Cloud point (6) and surface tension (7) determinations were made according to the American Society for Testing and Materials.

Results

Chemical analysis of the finished products was limited to determination of the hydroxyl value and the residual oxirane oxygen (8). These two quantities were indicative of the degree to which the reaction went to completion. The analysis of variance for hydroxyl values is shown in Table I. As can be seen, the catalyst level had a significant and independent effect. With the high catalyst level (0.30%) the mean hydroxyl value was 151.57 while the low catalyst level (0.15%) produced a mean hydroxyl value of 156.42. The samples with no benzene present as a cosolvent during the initial reaction period produced a mean hydroxyl value of 155.56 while those samples with benzene had a mean value of 152.43. This effect again was independent of the other variables. A significant two-factor interaction was also noted and is depicted graphically in Fig. 2, which shows hydroxyl value as a function of molar ratio and polyoxyethylene glycol molecular weight. The effect of varying the molar ratio seemed to be closely akin to that of varying the molecular weight of the polyoxyethylene glycol itself. This represents normal behavior for products of this type. Formulation errors involving up to 10% of either of the ingredients would not produce drastic changes in the properties of the materials thus produced.

The analysis of variance for the oxirane oxygen values is shown in Table I. As can be seen, significant factors involve the polyoxyethylene glycol molecular-weight effect and the catalyst-benzene interaction. Materials derived from polyoxyethylene glycol 300 had an average residual oxirane oxygen of 0.53% while PEG 400-derived products had 0.43% and the PEG 600 products, 0.28%. This corresponds to the decline in the initial oxirane oxygen content of the batch because of the dilution effect of the polyoxyethylene glycol, which is greater at higher molecular-weight levels. This therefore is a predictable variation. The catalyst by benzene interaction is shown in Fig. 3. It can be seen that the samples prepared with benzene as a cosolvent at the 30% level produced products with a higher over-all residual oxirane oxygen content than those in the neat system. This effect is sharply reduced at higher catalyst levels, thus indicating that the absence of benzene tends to promote the reaction and that catalyst concentration is important at high levels of benzene where the reacion is more sluggish. This may be at least in part owing to the tendency of the benzene to act as a diluent for the over-all reaction.

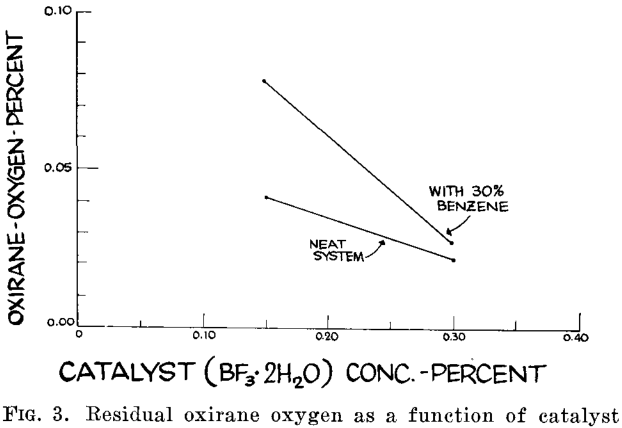

FIG. 3. Residual oxirane oxygen as a function of catalyst level.

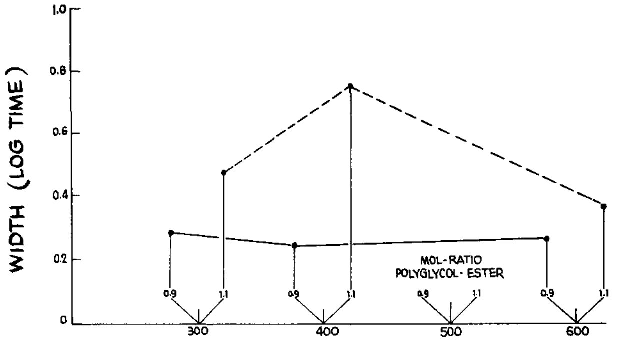

FIG. 5. Sinking time data. Log wetting time vs. log concentration width of 95% confidence interval about the line as a function of composition.

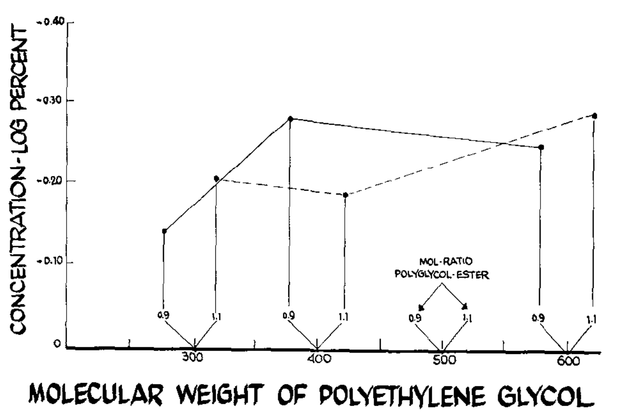

FIG. 6. Sinking time. Twenty-second intercepts of linear regression fits vs. molecular weight of polyglycol.

The cloud points of the polyethylene glycol 300- and 400-derived samples were too low to measure in aqueous systems. Those of the 600 samples were measured, and these determinations showed that molar ratio was the most important of the remaining factors in determining the cloud point. The 0.9:1 mol ratio gave a mean cloud-point of 52.75C, and the 1.1:1 mol ratio gave a mean cloud-point of 48.00C. These results are consistent with the hydroxyl value results discussed earlier.

The sinking-time data were subjected to linear regression analysis; the log-log slope of the sinking-time data versus concentration are depicted in Fig. 4 as a function of polyoxyethylene glycol molecular weight and molar ratio. There was a general tendency for the magnitude of the slope to decrease with the increasing molecular weight of the polyoxyethylene glycol. However these relationships were somewhat obscure particularly at the intermediate molecular-weight level. Previous work has indicated that the linear plot of log concentration versus log sinking-time, as normally expected, does not always hold (4, 9). Accordingly the 95% confidence intervals about the linear regression fit were determined and are depicted in Fig. 5. It can be seen that the lower molar ratio produces material with normal behavior throughout the molecular-weight range which was investigated while the sample with an excess of polyoxyethylene glycol gave rather large deviations from a linear fit. Second-order linear-regression analysis was also applied to the data but with a similarly poor fit.

By using the linear-regression fit, the 20-second intercepts of the log concentration versus log sinking-time plots were determined (Fig. 6). There was a general trend for the concentration necessary to produce 20-second wetting to increase with increasing molecular weight, but, like the slope data, the relationship was again rather obscure. Certainly the concentrations necessary for 20-second wetting (-0.10 to -0.30 log % or 0.8 to 0.5%) put these materials in the area of technically useful nonionic wetting agents.

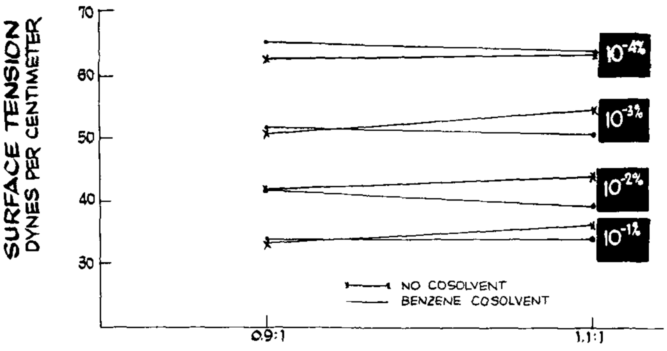

FIG. 7. Surface tension as a function of mol ratio.

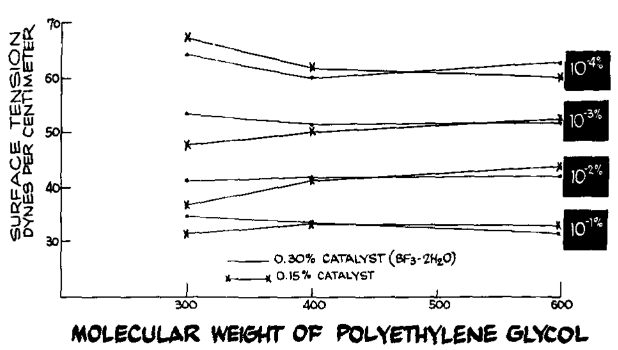

FIG. 8. Surface tension as a function of polyethylene glycol molecular weight.

TABLE II

Analysis of Variance Resume. Surface-Tension Data

Source of variation	Degrees of freedom	Mean square @ 0.100 %	Mean square @ 0.0100 %	Mean square @ 0.00100 %	Mean square @ 0.000100 %
Total	23				
Treatment	23	2.90	8.31	6.95	6.88
Molar ratio	1	6.30[a]	1.92	5.13	1.26
Catalyst level	1	2.34	8.64	19.62[a]	1.00
Benzene cosolvent	1	2.34	14.73	10.53	0.35
Type of polyglycol	2	0.74	17.01[a]	9.27	44.67[a]
Ratio × catalyst interaction	1	4.42	9.13	10.80	1.26
Ratio × benzene interaction	1	4.08	15.36	6.30	0.22
Ratio × polyglycol interaction	2	0.47	4.93	0.58	4.87
Catalyst × benzene interaction	1	1.87	4.86	2.73	6.30
Catalyst polyglycol interaction	2	5.92[a]	9.86	5.78	0.26
Benzene × polyglycol interaction	2	4.10	4.52	6.20	1.51
Residual (3 factor and higher)	9	2.55	7.10	6.79	5.03

[a] *Significant at 0.10 level of probability.*

Surface-tension measurements were made on aqueous solutions of the various materials at 25C. The analyses of variance were combined and are shown in Table II; the mean squares for each of the four concentration values are indicated. The data tend to indicate that the molar ratio by benzene and catalyst by polyoxyethylene glycol interactions are the important ones. The molar ratio by benzene interaction is indicated in Fig. 7. These data indicate that the presence of benzene is of little importance at the low molar ratio although it seems to benefit the system slightly in producing lower surface tensions at the high molar ratio. The catalyst by polyoxyethylene glycol interaction is shown in Fig. 8. This seems to indicate that the low catalyst level is beneficial, particularly at the more dilute concentrations.

ACKNOWLEDGMENTS

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