not accelerated by interrupting the reaction to release any carbon monoxide formed. This result does not agree with those of Hashimoto and Shiina (14) and indicates that carbon monoxide does not inhibit the homogeneous hydrogenation catalyzed by iron carbonyl. By analogy, the failure of sulfur compounds to act as poisons has been used as evidence that the catalytic reactions of metal carbonyls (37) and platinum salts (25) are homogenous.

The reduced fat products from the homogeneous hydrogenation catalyzed by iron pentacarbonyl are similar to those of heterogeneous hydrogenation. Therefore, the course of these two catalytic reactions may be similar. Metal carbonyls are well known for their ability to form complexes with conjugated dienes (3) and unconjugated dienes in which the ligand becomes conjugated (18). The findings of Hashimoto and Shiina (15), that iron pentacarbonyl acts as an isomerization catalyst to conjugate unsaturated fats in inert atmosphere, has been confirmed in this laboratory. This evidence suggests that conjugation may be a requirement for the homogeneous catalytic hydrogenation reaction. There is much evidence to indicate that conjugated unsaturated systems are required for homogeneous hydrogenation (8,13,19,21). Therefore, a catalyst that isomerizes fats and also activates hydrogen should be one of the best ways to achieve homogeneous hydrogenation. Conjugation may also be an important process in heterogeneous catalytic hydrogenation of fats. The formation of conjugated intermediates during heterogeneous hydrogenation of fats has been demonstrated and suggested previously (1, 6,9,35). The greater susceptibility of these conjugated forms to hydrogenation and isomerization into unconjugated isomeric forms would account for their limited accumulation in hydrogenated fats.

ACKNOWLEDGMENT

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New Nonionic Detergents Derived from Epoxidized Oils[1]

K. L. JOHNSON, Swift & Company, Research Laboratories, Chicago, Illinois

Abstract

A new class of nonionic detergents derived from epoxidized oils having an oxirane oxygen content of 6–10% is discussed. Their mol wt and micellar wt distributions, as studied in the ultracentrifuge, are presented and cited as partial explanations for their unique properties as compared to conventional nonionic detergents such as ethoxylated alkyl phenols. Critical micelle concentrations (CMC) determined by light scattering data are presented.

Discussion

The micellar structure and detersive ability for two families of derivatives are studied as a function of the weight percent of the polyoxyethylene hydrophil. The evaluation of these materials as emulsifiers, detergents, and lubricants is presented, with some theoretical reasons for their performance. Surface tension, foaming, and wetting characteristics are also given a comparative evaluation, and some second generation derivatives are briefly discussed.

The unique behavior of these materials as foaming agents, effects on surface tension, broad utility as emulsifiers, and unusual performance in scattering light, are explained by their broad distribution of molecular weight as verified by the ultracentrifuge. The broader distribution of mol wt is, however, not the whole story. The magnitude of the mol wt, being from 4–10 times as great as the materials currently available in this area, undoubtedly affects their properties. Perhaps these materials will do more efficient jobs in applications where the present nonionic detergents perform poorly.

During the past decade, the growth of the plastics industry and its attendant technology have resulted in the commercial production of a great many new materials. It is inevitable that the availability of such materials results in their application to other areas, e.g., the introduction of epoxidized unsaturated vegetable oils and their derivatives. These materials, designed primarily as combination plasticizer-stabilizers in plastic films and coatings, have made commercially available polyfunctional chemicals from which the organic chemist can fashion unique new molecules for a variety of applications.

Chemistry

The polyfunctionality of these materials and the wide spectrum of reactions that they may undergo

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[1] Presented at the AOCS Meeting, New Orleans, La.

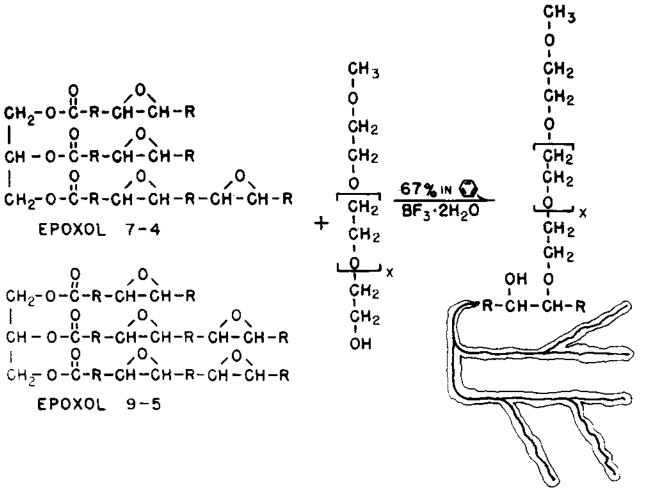

FIG. 1. Reaction used to prepare derivatives studied in this series of tests. (Diagram at right was roughed out to preserve simplicity.)

makes them valuable to the research chemist searching for new products. The main reaction under study here is the alcoholysis of epoxidized soybean oil and epoxidized linseed oil carried out in the presence of a Friedel-Craft's catalyst to yield 1, 2-ether alcohols (Fig. 1). If a polyoxyethylene alcohol is chosen as the major reactant, we arrive at a product which can be made to exhibit varying degrees of water and oil solubility as the chain length of the polyoxyethylene alcohol is varied.

The oils studied were: commercial epoxidized soybean oil, Epoxol 7-4, having an oxirane oxygen level of ca. 7 wt %; and epoxidized linseed oil, Epoxol 9-5, having an oxirane oxygen level of ca. 9 wt %. The polyoxyethylene alcohols were mostly monomethyl ethers of polyoxyethylene glycols, prepared in cooperation with the Nitrogen Division of the Allied Chemical Corp. in mol wt ranging 150–1050 in increments of ca. 150. A number of these materials are available from a variety of suppliers. Since the polyoxyethylene alcohols and the epoxidized oils were not always mutually miscible, the reaction was carried out in the presence of benzene at ca. 33%. This prevented droplets of the oils from forming and subsequently polymerizing on their surface, thus avoiding grainy insoluble polymeric material in the finished product. The reaction temp during the synthesis was held at 50C or lower. The benzene was effectively removed as an azeotrope by adding distilled water to the reaction mass and stripping off the volatile components at a pressure of 150 μ absolute in a rotating type evaporator. The evaporator flask was maintained in a water bath at 70C.

TABLE I

Use of Isopropyl Alcohol to Inhibit Polymerization at Stoichiometric Ratio and with Excess Oxirane Oxygen (Deficiency of Polyoxyethylene Alcohol)

Epoxidized oil employed	Conditions to inhibit polymerization	Mean mol wt	Standard deviation of distribution
Epoxol 7–4	10% mole excess of polyoxyethylene alcohol	2,760	2,900
Epoxol 7–4	10% mole excess of isopropyl alcohol	2,260	3,000
Epoxol 9–5	Isoproyl alcohol used as reaction solvent	2,830	3,300

The control of random polymerization by the presence of a secondary alcohol which reacts with any excess oxirane oxygen after the majority of the more reactive primary alcohol has been consumed. Differences in solubility were qualitatively noted with the Epoxol 9–5 derivative exhibiting the highest solubility.

A 10% mole excess of the polyoxyethylene alcohol insured that the resulting material would be essentially monomeric. This also allowed for minor variations in the mol wt of the polyoxyethylene alcohol and the oxirane oxygen level of the oil. Ultracentrifuge studies showed that the mol wt distribution had an unusually large standard deviation, indicating that some higher polymers had formed. But mean values were close enough to those expected to indicate that these derivatives did not predominate. The unreacted glycol also contributed to these figures. The hydroxyl group formed in the alcoholysis inhibited further reaction by the steric hindrance of the bulky polyoxyethylene chain adjacent to it, and because it was a less reactive secondary hydroxyl group as opposed to the primary hydroxyl group on the terminal end of the unreacted polyoxyethylene chain. This excess would probably be indicated in a commercial application as the mol wt of the polyoxyethylene ethers and the oxirane oxygen level of the oils generally vary slightly from different batches and suppliers.

An alternate method of controling the mol wt is to use slightly less than the stoichiometric amount of polyoxyethylene alcohol, and to have a secondary alcohol, such as isopropyl, present to react with the remaining epoxy groups after the primary alcohol groups and the polyoxyethylene alcohol have undergone reaction. The secondary hydroxyl group on the polymerized material does not react as rapidly as the isopropyl alcohol inasmuch as the steric hindrance serves to suppress this side reaction. This is substantiated by data in Table I.

The catalyst used in most of the preparations was the dihydrate of boron trifluoride. This material was extremely easy to handle and appeared to function as well or better than other materials. The most active catalyst evaluated was antimony pentachloride, but it produced a dark product. Tin tetrachloride and various boron trifluoride complexes were tested

TABLE II

Mol wt (Calculated)	Surface tension ASTM D1331-56				Interfacial tension hexane/water				Interfacial tension benzene/water			
	$10^{-1}\%$	$10^{-2}\%$	$10^{-3}\%$	$10^{-4}\%$	$10^{-1}\%$	$10^{-2}\%$	$10^{-3}\%$	$10^{-4}\%$	$10^{-1}\%$	$10^{-2}\%$	$10^{-3}\%$	$10^{-4}\%$
Epoxol 9–5 Series												
1655	I	I	I	I	I+	I+	I+	I+	3.6*	8.2*	13.7*	24.3*
2465	I	I	47.2	63.4	I+	I+	10.7	25.7	4.4*	9.0*	13.3*	22.5*
											14.8	25.6
3060	39.3	44.6	57.3	65.2	0.3	6.4	19.8	28.6	2.0	10.1	16.6	24.4
3990	41.7	45.1	55.5	66.5	5.8	6.2	12.8	23.2	1.4	6.2	12.8	23.2
4925	42.7	47.5	58.8	67.2	8.2	9.9	21.5	29.2	4.6	8.0	14.1	24.2
5500	42.8	47.2	58.3	68.2	6.3	10.1	21.1	28.5	3.8	8.3	14.3	23.5
6550	44.7	48.9	57.5	63.3	7.9	12.9	22.3	28.1	1.0	4.9	13.0	20.6
Epoxol 7–4 Series												
1540	I	I	I	I	2.0*	9.0*	18.9*	28.9*				
2080	I	I	I	I	I+	I+	I+	I+				
2550	I	I	56.7	66.9	I+	I+	23.1	30.8				
3120	42.1	43.9	55.8	60.5	4.2	7.0	15.6	22.1				
3920	40.4	42.4	56.4	63.9	2.7	5.3	15.8	24.9				
4340	42.0	45.6	56.2	64.6	2.9	5.5	20.0	24.9				
5080	43.4	46.8	58.5	64.5	6.8	10.1	18.7	26.7				

I—Sample insoluble
*—Sample dissolved in non-aqueous solvent

+—Sample insoluble in both phases

All values are the average of three readings

Data obtained from surface and interfacial tension tests. Graphical interpretation resulted in a series of lines that intertwined and were generally difficult to sort out.

TABLE III

Mol wt (Calculated)	Wt % ethylene oxide	Physical state	Water solubility	Ultracentrifuge data		SD / mol wt
				Mol wt (wt avg)	SD of distribution	
Epoxol 9–5 Series						
1655	42%	Liquid	I	6,900	10,700	1.55
2465	61.4%	Liquid	SIS	2,390	3,600	1.51
3060	69.0%	Liquid	S	3,050	4,200	1.38
3990	76.4%	Liquid	S	2,970	3,400	1.14
4925	81.0%	Gel	S	3,420	3,900	1.14
5500	83.0%	Paste	S	2,680	3,900	1.46
6550	85.5%	Solid	S	5,800	8,500	1.46
Epoxol 7–4 Series						
1540	32%	Liquid	I	3,750	6,400	1.71
2080	52%	Liquid	I	4,500	5,900	1.31
2550	59%	Liquid	SIS	2,530	4,500	1.78
3120	70.5%	Liquid	S	3,110	7,000	2.25
3920	73.5%	Gel	S	2,670	3,100	1.19
4340	76%	Paste	S	2,850	5,900	2.11
5080	81%	Solid	S	3,380	5,700	1.68
3920 (Rerun)	73.5%	Gel	S	3,490	5,900	1.70
Conventional Nonionic Detergents						
Solar 15	73%	Liquid	S	968	108	0.11
Igepal DM-730	73%	Gel	S	1,535	330	0.21

Physical properties of the two families of condensates compared to those of two conventional nonionic detergents.

for catalytic activity. The only boron trifluoride complex that was found to exhibit inadequate activity was that of urea.

Tests showed that raising the kauri-butanol value of the solvent lowered the requirements for the solvent level only slightly, while making the conditions at which the material has to be purified much more vigorous. Toluene, xylene, and several dry commercial aromatic naphthas were, however, found to produce satisfactory results and could be used if the removal of the solvent was not necessary in any given application.

Physical Characteristics

The methoxypolyoxyethylene glycol derivatives prepared in both families are essentially what would be expected (Table III). Materials prepared by condensing the higher mole wt polyoxyethylene alcohols ranged in physical form from pastes to waxy solids which could be liquefied by the addition of a small amount of water. Materials from lower mol wt polyoxyethylene alcohols were viscous liquids. Relative solubility was, as might be expected, dependent on the mol wt of the polyoxyethylene alcohol used in the condensation. The products ranged in color from a dark yellow-red for the low mol wt materials to a light amber for those of higher mol wt. The addition of small amounts (1–4%) of various bases such as alkanolamines, after the reaction was complete, improved the color and inhibited further darkening. Excessive heating during the reaction also resulted in a darker product. The color was probably caused by unstable minor products of side reactions involving the boron trifluoride or its decomposition products.

Light Scattering Data

These materials were examined over a range of concentrations to learn if the CMC could be determined by light scattering techniques. Lower members of the series did not disperse well enough to give meaningful results. Higher members all gave essentially straight lines passing through the origin (Figs. 2, 3) indicating that there was no sharply definable CMC. This might have been expected inasmuch as the materials have a broad distribution of mol wt. In nonionic detergents, as the distribution of mol wt becomes broader, the tendency is for the CMC to become a less clearly defined point. Subsequent studies in the ultracentrifuge indicated that at a 1% concn and an apparent mol wt of 2,580 there were an average of 65 molecules per micelle, while at an apparent mol wt of 1,880 there were an average of 51 molecules per micelle. These mol wt were determined by equilibrium ultracentrifugation as described by Donnelly (1). Standard deviation of the micellar weights were greater in magnitude than the weight of the average micelle, indicating that a very broad spectrum of micellar species was present.

Surface Tension Data

The data on surface tension (2) as a function of concentration gave results in agreement with those for light scattering experiments. Here again the break that one normally expects in the plot of surface tension with respect to the concentration when plotted on the semilogarithmic basis failed to materialize. This supports the earlier conclusion that this material shows no clearly defined CMC (Fig. 4). More surprising, however, was the fact that the family of lines formed in the plot of surface tension with respect to concen were not clearly defined parallel lines, but rather appeared to be the result

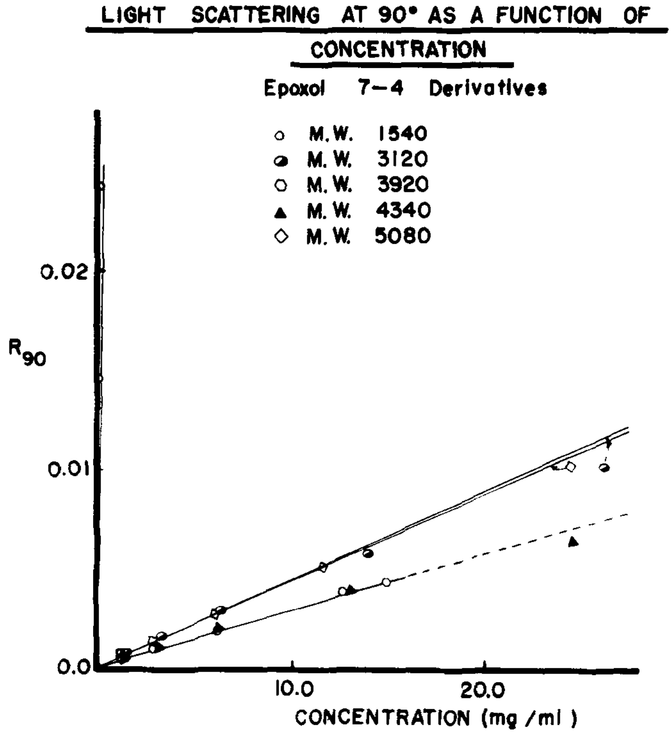

FIG. 2. Behavior of the methoxypolyoxyethylene alcohol derivatives of Epoxol 7–4. The plots all appear to pass through the origin with no abrupt curvature changes to indicate a critical micelle concentration.

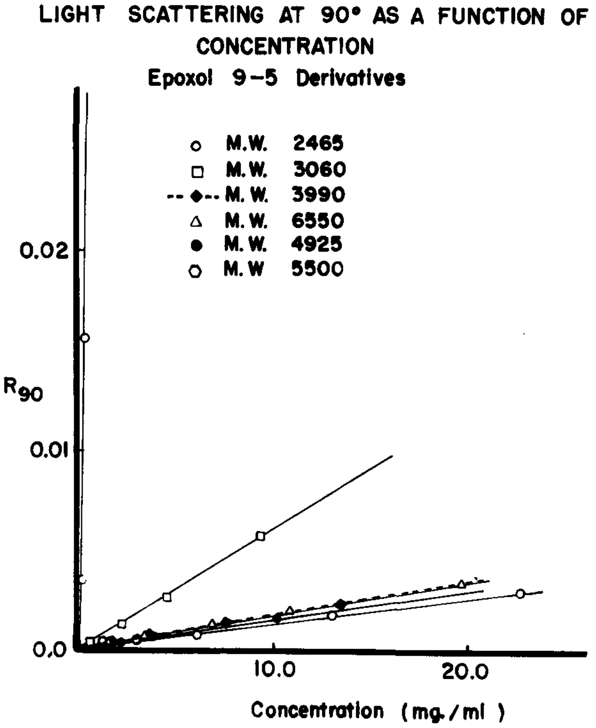

FIG. 3. The same behavior noted for the Epoxol 7-4 derivatives is exhibited for the Epoxol 9-5 derivatives. The low mol wt derivatives were hard to work with in preparing aqueous dispersions.

of experimental noise around a single line (Table II). This was unexpected, and its full significance is not fully understood. It may be, however, that at the surface of the solution one particular species predominates and the nature of this species is essentially independent of the mol wt of the polyoxyethylene alcohol used to prepare the sample. Interfacial tension data for benzene-water systems and hexane-water systems behaved in a slightly different manner, showing a maximum at a given mol wt for each system. There were areas in both families where the detergents were insoluble in both hexane and water, probably because of their high mol wt. No such difficulty was encountered with the benzene samples. The interfacial tension values obtained by dissolving the detergent in the aqueous phase, as opposed to dissolving it in the nonaqueous phase, appeared to be essentially the same.

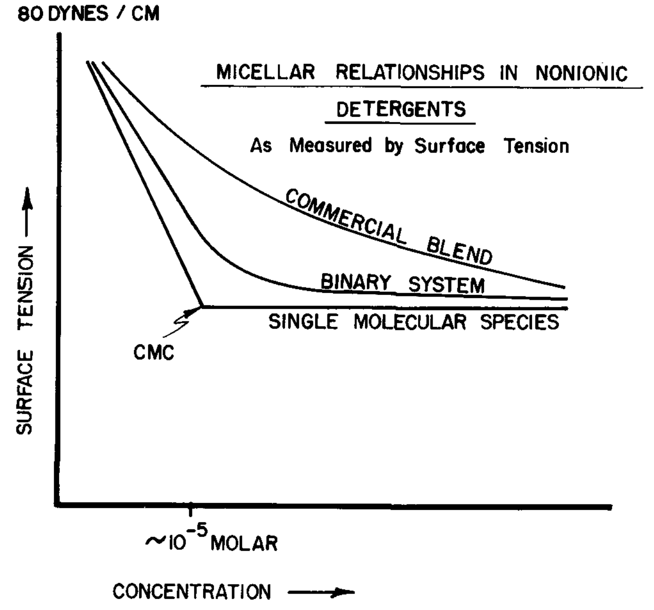

FIG. 4. Loss of definition of the break in the surface tension vs. concn curve in going from monodisperse to increasingly polydisperse systems as proposed by Reich (*6*) is shown empirically above. As data in Table II indicate, these newer derivatives carry this trend to its obvious conclusion—a straight line (3). This is in agreement with the light scattering data in Figures 2, 3.

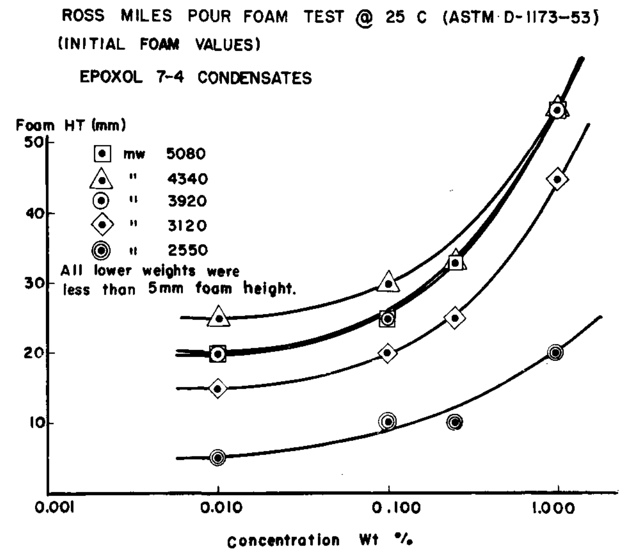

FIG. 5. Foam height of the Epoxol 7-4 condensates. This graph is well behaved with foam height increasing with mol wt (and HLB) until it levels off at a mol wt of 4,000–4,500 and falls back to a lower value.

Foaming Data

The foaming tendency of these materials (4) is sharply reduced compared to other similar systems. This is explicable by the fact that the molecular configuration is such that many hydrophilic portions are attached to a hydrophobic nucleus. The formation of a lamellar film from such a species is difficult because the correct mol orientation is somewhat unstable. The foam of some of the derivatives, particularly those in which an alkyl phenyl group replaced the methyl group at the ether end of the polyoxyethylene chain, proved to be very stable, though at a much reduced level. In some cases the latter materials were even able to withstand the defoaming effect of silicone oils after a short period. Presumably, they were able to emulsify these oils to such an extent that they no longer functioned as defoamers.

The derivatives of epoxidized soybean oil exhibit predictable foaming characteristics. The foam height increases with increasing mol wt; hence the attendant increase in the HLB of the system (Fig. 5). The derivatives of epoxidized linseed oil form a family of curves which were not readily interpretable in a simple graphical form (Fig. 6). However, when foam height is plotted as a response surface with respect to concn and mol wt, a smooth surface appears with a maximum foam height appearing at the center of the system (Fig. 7). The foam height ridge through the response surface is not, as one might expect, a straight line following a given mol wt. Rather, it shows a slight curvature with higher foam coming at higher mol wt in the lower range of concn. This again suggests a possible fractionation of species at the interface.

Emulsification Data

The performance of the two groups of materials as

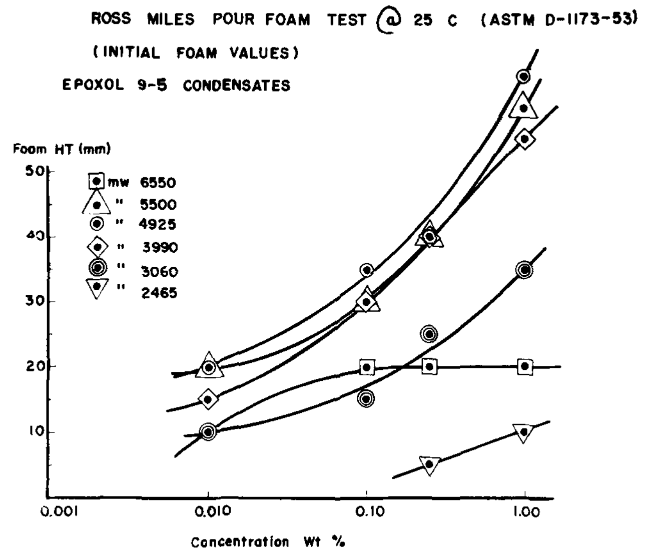

FIG. 6. Epoxol 9–5 derivatives show seemingly less order than Epoxol 7–4 derivatives.

emulsifiers was compared to that of ethoxylated nonyl phenols. They were tested in a system buffered to a pH value of 12.0 and containing 49.5 parts water, 49.5 parts oil and 1 part emulsifier. Dye was added to the oil phase to help identify the samples and to define more sharply the line between the creamy phase and a phase that had "oiled" out. This was an effective method of testing. In each case, the system was allowed to come to equilibrium by shaking for 2 hr on an Eberbach automatic shaker, then standing for 24 hr. The samples then were put in 100-ml graduated cylinders, given a total of 30 inversions, and photographed. They were photographed again after standing 2 hr. This gave a comparison of immediate performance and stability of the various samples. In both cases, the materials proved to have a much broader utility as emulsifiers with respect to ethylene oxide content. This was particularly true with aromatic hydrocarbons as typified by benzene (Figs. 8–11).

The epoxidized soybean oil at the lower oxirane oxygen level produced derivatives with an apparent

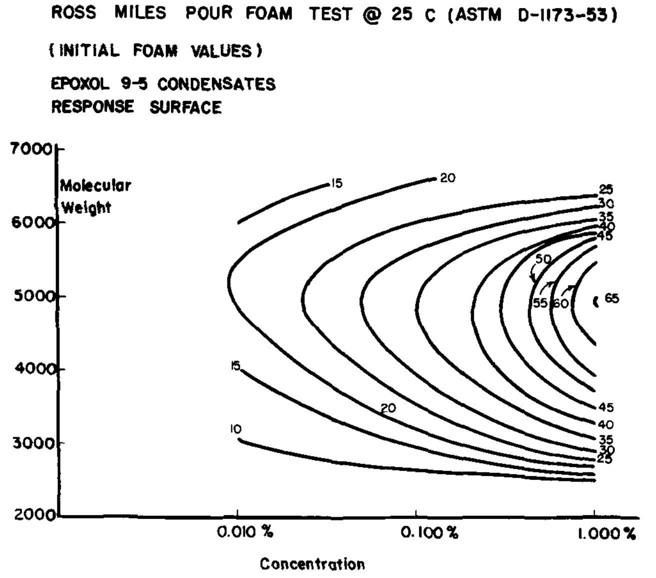

FIG. 7. Condensates of Epoxol 9–5 gave a family of curves which was not as ordered as those from Epoxol 7–4. However, when foam height was plotted as a response surface with respect to mol wt and concn, it again assumed the orderly pattern shown here.

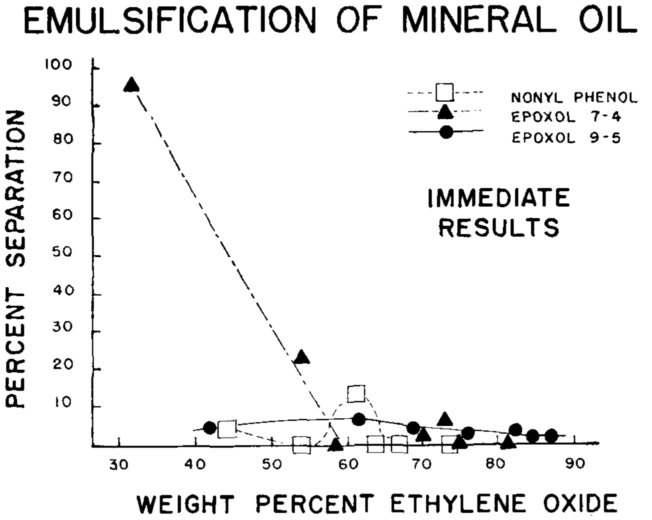

FIG. 8.

wider range of utility than those from the epoxidized linseed oil. This may indicate the optimum oxirane oxygen level is between 7%–9%. The number of hydrophilic groups per molecule also would have bearing on their performance as emulsifiers.

The broad distribution of mol wt would again play an important role in making the materials wider-spectrum emulsifiers. It is known that, in the case of ethoxylated alkyl phenols, the commercial mixtures of mol wt caused by the variation in wt of propylene polymer on one end of the molecule, and in the wt of the ethylene oxide polymer on the other, have superior emulsification ability compared to similar materials with the same empirical formula prepared in the laboratory and having precise composition and hence exhibiting essentially no deviation from the expressed mol wt.

Emulsion Particle Size Distribution

A series of tests were set up with a Coulter Counter (5) in an attempt to ascertain the effect, if any, of the polydisperse character of the emulsifiers and their micellar solutions upon emulsion particle size distribution. A series of three commercial ethylene oxide condensates of nonyl phenol having 54%,61%, and 65% ethylene oxide and marketed as Solar 53, NPO, and NP, respectively, were used as standards indicative of nonionic emulsifiers most commonly encountered. Three derivatives of epoxidized soybean

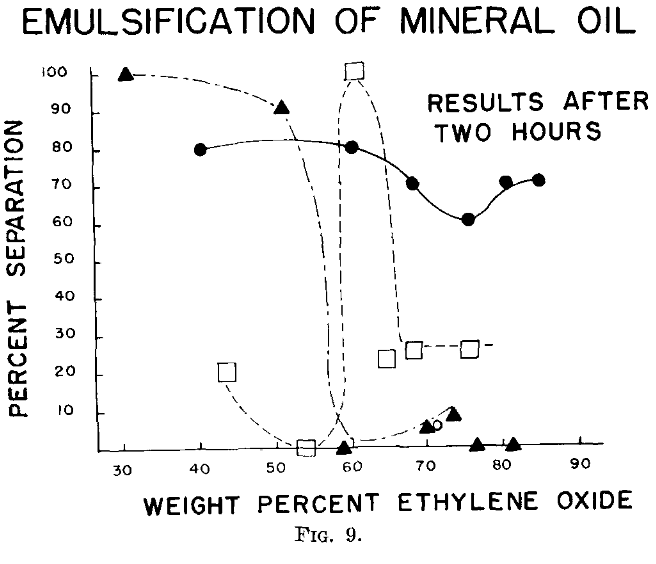

FIG. 9.

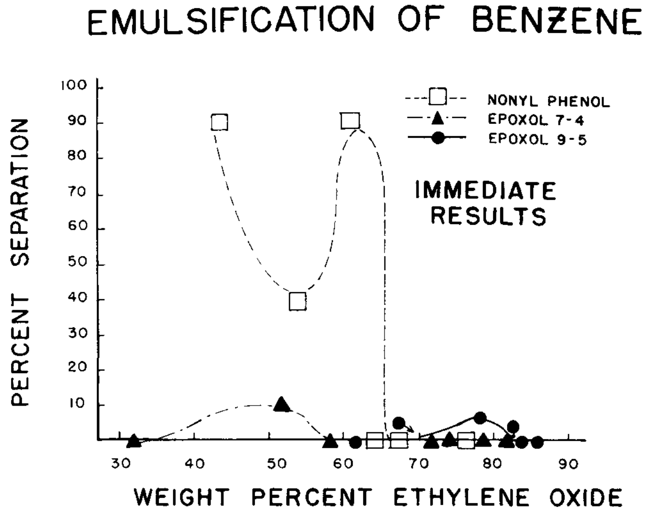

FIG. 10.

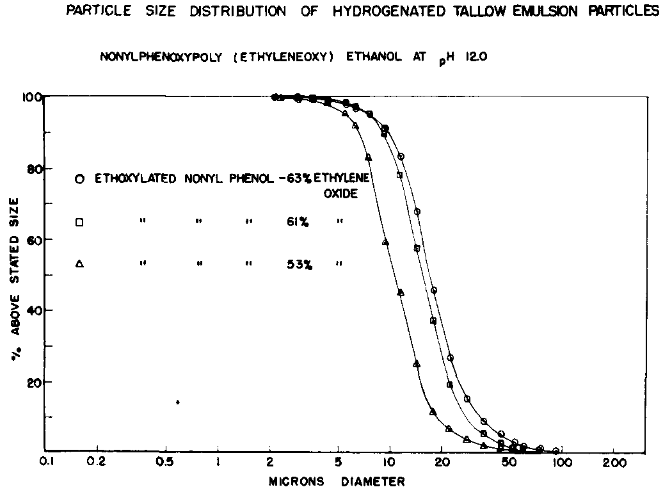

FIG. 12.

oil based on the methoxypolyoxyethylene alcohols and having theoretical ethylene oxide contents of 52%,59%, and 70.5% were selected as being representative.

Test solutions were prepared by heating to 70C a mixture of 188 g water buffered to 12 pH, 10 g of 58C titre hydrogenated tallow, and 2 g of test emulsifier. This blend was then agitated for 10 min at maximum speed on a Hamilton Beach Model 30 mixer. After 10 min the emulsions had cooled to slightly below 50C, indicating that the internal phase (hydrogenated tallow) had already solidified. It was assumed that no change in the size distribution of these solidified particles would occur upon aging; hence, they were not given priority over other samples awaiting analysis. This resulted in a time lag of ca. 8 weeks between sample preparation and the analysis.

Results of the tests with the nonyl phenol ethylene oxide adducts showed that the particle size, within the interval of the test, showed a relatively narrow distribution and a decrease proportional to the decrease in ethylene oxide content (Fig. 12). Results from the methoxypolyoxyethylene alcohol adducts of epoxidized soybean oil were, however, quite different. These data showed that anomalous breaks occurred in each of the three curves. These breaks remained upon rechecking and appeared to represent an actual bimodal character in the distribution. It was postulated that the lower and smaller of the two modes might possibly represent the apparent electronic size of agglomerations of emulsifier (Fig. 13).

To test this theory, a series was set up in which samples were prepared from the same emulsifiers, leaving out the hydrogenated tallow. These were aged for 8 weeks at room temp during which time they became slightly hazy. This was conceivably due to partial hydrolysis of the glyceride linkages, although no loss in surface activity was noted with respect to surface tension measurements and foaming tendency which stayed at its previous low level. These samples did produce detectable particle size measurements with modes roughly corresponding to those of the lower and smaller modes in the earlier tests (Fig. 14). This, plus the fact that the earlier tests with the ethoxylated nonyl phenols did not exhibit any anomalous data, led to the conclusion that the higher mode in the earlier series of tests represented the mode of the particle size distribution of the emulsion particles.

Using this assumption, the graph showing the particle size distribution was plotted, using values extrapolated from the Log-Log Cumulative Frequency Plot. The curves thus obtained were so close as to indicate that they represented three separate estimations of the same value (Fig. 15). The slope of the composition vs. log diam curve indicated a slightly broader distribution than that obtained by the use of the ethoxylated nonyl phenols and having a slightly

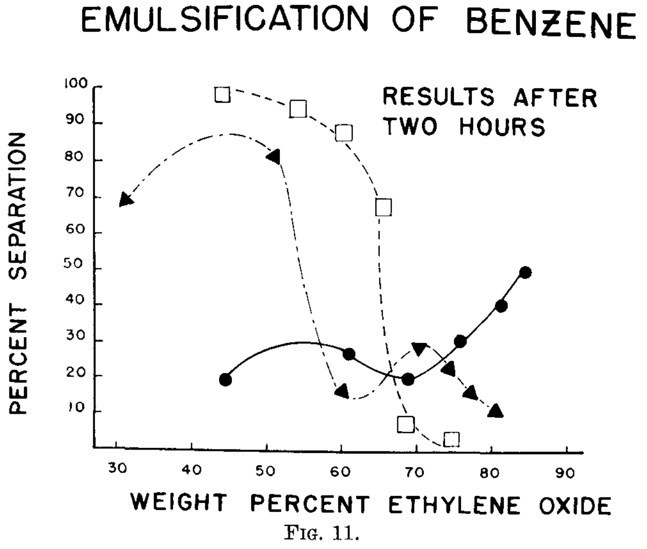

FIG. 11.

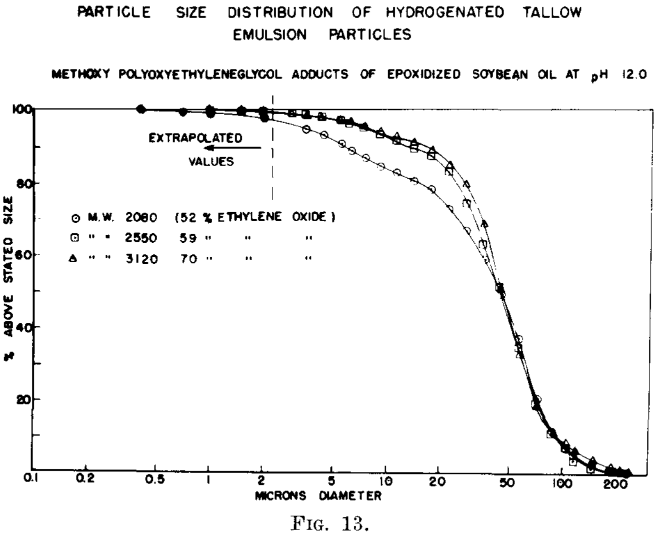

FIG. 13.

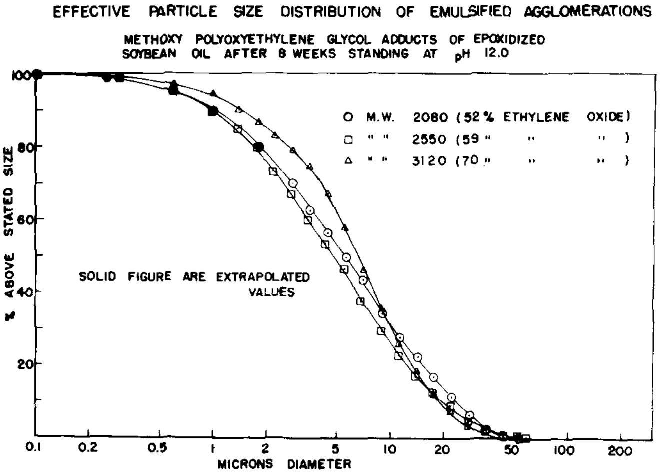

FIG. 14.

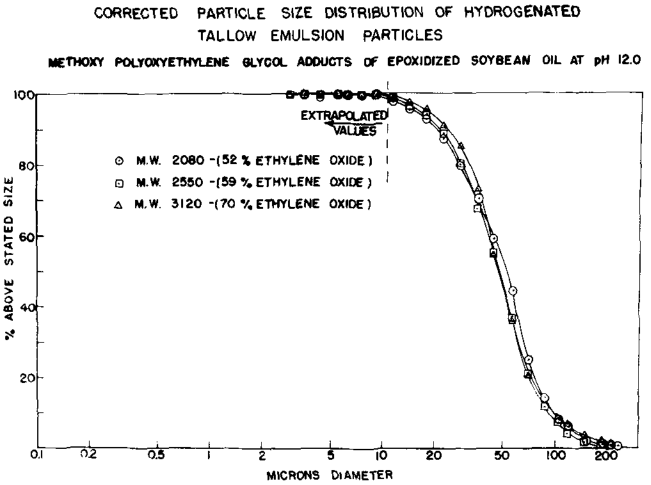

FIG. 15.

larger average particle size. This seems to be another example of a property which, while it would be expected to, does not vary while the mol wt varies.

Ultracentrifuge Data

Much has been attributed to the broad distribution of mol wt that these samples were supposed to exhibit. To test this hypothesis, the entire series of 14 derivatives were subjected to measurement of their equilibrium ultracentrifugation behavior at 25C, using isopropyl alcohol as a solvent to determine their mean mol wt, and the standard deviation of their distributions (1) (Table III). Results indicated that some of these materials do have mol wt very close to those predicted by the chemistry of the reaction. It appears, however, that there is a factor giving rise to higher than predicted mol wt at the lower level, and lower than predicted mol wt at the higher level. The best explanation for this behavior rests on the fact that the equivalent concen of the reacting species and the species for competing reactions is lower in the latter than in the former case. This effect was also noted in that the reaction velocity appeared to be greater at the lower mol wt level in spite of lower catalyst concentrations. Appreciable levels of water in the reactants could lead to the formation of unhindered secondary alcohol groups on adjacent carbon atoms, which could conceivably result in polymerization and similarly anomalous mol wt, but the order of most of the differences indicated a more systematic reason. A definite source of random error can be pinpointed by the disparity between the two determinations run on the Epoxol 7-4 derivative of calculated mole wt 3920. The reason for this can be appreciated by examining the Schlieren photographs obtained from the ultracentrifuge for this sample, and comparing it to the picture obtained from the paucidisperse emulsifier Solar 15 (Fig. 16). One necessary datum is the intersection of the sedimentation curve with the line in the Schlieren pattern corresponding to the outer edge of the spinning column. This is quite readily estimated with the mono- or mono-paucidisperse materials, whereas in the case of these new polydisperse moieties, the sedimentation curve is practically asymptotic to this line. As can be seen from the data, the SD of the mol wt distribution are all significantly greater than those of the more commonly used nonionics even when taking the differences in mol wt into consideration. The deviation of the mol wt was larger than one would expect on the basis of entirely random polymerization.

In reacting these materials to produce detergents, there are essentially 5 degrees of freedom in the variation of mol wt in the case of the epoxidized soybean oil derivatives, and 6½ in the case of epoxidized linseed oil. These possibilities for deviation lie in the distribution of species in the epoxidized oil and the distribution in mol wt of the polyoxyethylene alcohol at each of the possible reaction sites on the triglyceride. It is evidently these possibilities for variation that result in the broad distribution of mol wt that is observed.

Practical Applications

The use of these materials is suggested in the agricultural chemical field, where aromatic naphthas are commonly utilized as solvents for insecticides. They should show the same synergism with the calcium sulfonate and amine sulfonate emulsifiers often used in combination with nonionic detergents in agricultural emulsifiers. Their structural similarity and their proven ability to emulsify fatty materials could possibly lead to their use in the wool-scouring or other textile-processing fields. Their unique polyfunctionality, in that they possess a multiplicity of ester linkages coupled with their water solubility,

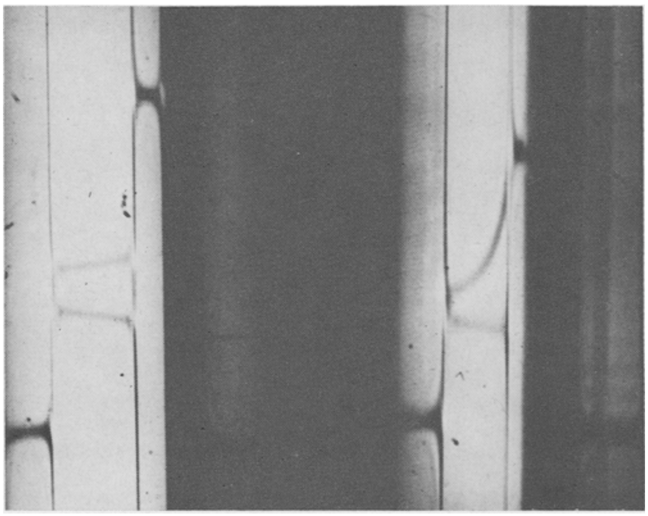

FIG. 16. Two Schlieren photographs taken in the ultracentrifuge and comparing the mol wt distribution of Solar 15, a 15 mole ethylene oxide adduct of nonyl phenol, with that of Epoxol 7–4 condensate with the polyoxyethylene alcohol having mol wt 3920. The distribution curve for Solar 15 is practically a straight line, indicating paucidispersity, whereas that for the condensate is practically asymptotic to the outer edge of the spinning column.

would indicate their usefulness in aqueous or nonaqueous lubricants. They also seem to have some use as viscosity control agents in such systems. The lubricity of the alkylphenyl ether or ester derivatives, even at relatively dilute concentrations at a metal-metal interface, is remarkable. They will provide useful lubrication at pressures from 2–2½ times as great as that provided by comparable soap solutions widely used in the wire drawing and metal extruding industries. In addition, their nonionic character would probably eliminate the buildup of sludge in such systems, particularly in the drawing of copper tubing and wire.

Derivatives prepared by substituting alkylphenyl group for the methyl group at the hydrophobic end of the polyoxyethylene alcohol show promise as textile lubricants to prevent the balling of fabrics in presses. It is also expected that they would impart a better hand to the fabric due to their many ester groups which seem to be useful in this respect. The low foaming characteristics of the methyl ethers could lead to their use in heavy duty power washing. Inasmuch as there are functional groupings present after the products have been formed, their use as chemical intermediates is also suggested. One interesting family of derivatives is that prepared by splitting the triglyceride formed with a primary or secondary amine. The diethanolamides of these materials formed in this manner exhibit unique properties in that, while still being diethanolamides, the resulting products have more greatly reduced effects on the viscosity of aqueous solutions than do the corresponding derivatives of saturated fatty acids or unsaturated fatty acids. Their use as chemical intermediates has, however, of this date been just barely investigated.

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Chromatographic Analysis of Sucrose Esters of Long Chain Fatty Acids

HIROYUKI MIMA and NOBUYUKI KITAMORI, Research Laboratories, Takeda Chemical Industries, Ltd., Osaka, Japan

Abstract

The procedure of the quantitative analysis of the components of sucrose ester products is described. By thin-layer chromatography, sucrose ester products have been separated into their components: mono-,di-,tri-, and higher esters. The individual components have been extracted from the plate and determined colorimetrically by using anthrone reagent. Standard substances of monoesters, diesters and triesters, which have been synthesized from gas-chromatographically pure methyl esters of fatty acids, have been isolated by column chromatography and identified by elemental analysis, colorimetric determination and N.M.R. determination.

Introduction

Recently, nonionic surfactants have been developed and a number of studies of their physical properties have been reported. In most of these surfactants, hydrophilic properties are due to polyoxyethylene chains, which have a range of molecular weight distributions. It is almost impossible to obtain surface-chemically pure samples from such surfactants.

In 1956, sucrose esters of long chain fatty acids, such as sucrose laurate, myristate, palmitate, and stearate were prepared by Osipow et al. (1). These esters have a hydrophilic group of definite molecular structure, viz., a sucrose residue. This will permit a supply of pure samples for further studies of the physicochemical properties of nonionic surfactants.

As in usual organic reactions, it is assumed that the preparation of pure monoesters or diesters is not obtained. Therefore, mixtures of sucrose, sucrose monoester, sucrose diester, and others must be formed. To obtain pure samples, fatty acid methyl esters must be purified and sucrose ester products separated into their components. Consequently, before syntheses of sucrose esters, fatty acid methyl esters were purfiied by distillation and gas-chomatographically pure methyl esters were obtained. By using these methyl esters, sucrose esters were prepared and pure mono- or di-esters were isolated by silica gel column chromatography.

In the early stages of study on the synthesis of sucrose esters, it was believed that sucrose, which was the raw material for these esters, was the lowest cost hydrophilic group available for use in the preparation of nonionic surfactants (2). To manufacture sucrose esters at low cost it is necessary to examine the conditions of manufacture and to control the product. For these purposes, an easy and accurate method to analyze sucrose ester products was required.

Only one method for the analysis of sucrose ester has been reported (1). This method, however, requires large samples and must be carried out with the assumption that sucrose ester products contain sucrose, mono- and di-esters, and no tri- and higher esters.

The quantitative determination of the components of sucrose ester products was accomplished by a minor modification of TLC described by Vioque et al. (3).

Experimental

Samples. Sucrose esters were synthesized by Osipow's method from gas-chromatographically pure methyl esters of fatty acids.

Anthrone Reagent. Anthrone was dissolved in con-