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The Effect of Mole Ratio Distribution on the Physical Properties of a Polyoxyethylated Alkylphenol

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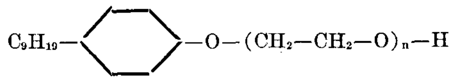
THE ease with which the physical properties of the polyoxyethylated nonionic surface active agents may be slightly or even radically altered by varying the number of ethylene oxide groups makes them widely applicable to numerous industrial processes. There is a certain amount of literature (1, 2, 3) readily available to show that a certain hydrophobe-hydrophile balance (i.e., average mole ratio of ethylene oxide to base material) is required to obtain maximum wetting, optimum detergency, emulsification, demulsification, water or hydrocarbon solubility, certain foam or non-foam characteristics, etc. It has occurred to us that the hydrophobe-hydrophile balance may be greatly affected not only by the average mole ratio of ethylene oxide to the hydrophobic material but also by the distribution of the various molecular species which make up the average mole ratio.

Discussion

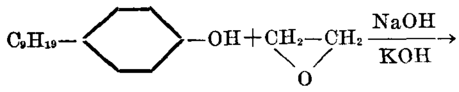
As an introduction to the discussion of our actual experimental data, a reiteration of certain fundamental facts concerning the nonionic surfactant with which we have dealt is necessary. "Surfactant" is an increasingly popular abbreviated name in the trade for a surface active material.

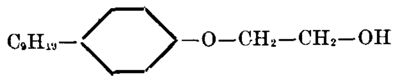
The polyoxyethylated alkylphenol which we used for our experimentation is a typical member of the polyoxyethylated nonionic surfactant class. Its structure may be represented:



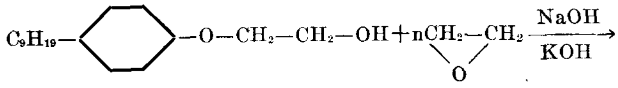
The nonylphenol group, being hydrocarbon in nature, represents the hydrophobic portion of the molecule. The average length of polyoxyethylene chain, which represents the hydrophilic end of the molecule, can be varied to produce almost any hydrophobe-hydrophile balance which one may desire. This is one of the most interesting features, and by far the most important one for this type of surfactant. By simply varying the ratio of ethylene oxide units to nonylphenol, it is possible to prepare compounds which vary from water insoluble-mineral oil soluble products to those which are infinitely soluble in water and completely insoluble in most hydrocarbons.

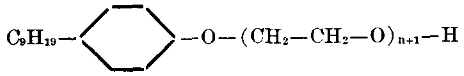
In the reaction used for the preparation of these compounds the addition of the first ethylene oxide to the nonylphenol base is accomplished almost quantitatively before further polymerization occurs:





This is due to the fact that the nonylphenol hydrogen is more reactive than the resulting nonylphenoxyethanol hydrogen. However after completion of the first reaction, chaining out of the ethylene oxide begins:





Since this further reaction is a random one, it becomes obvious that a single compound is not obtained but a mixture of closely related materials.

Flory (4) has made an exhaustive study of the addition of ethylene oxide to ethylene glycol and observed that the number of molecules of varying size is represented by Poisson's distribution formula.

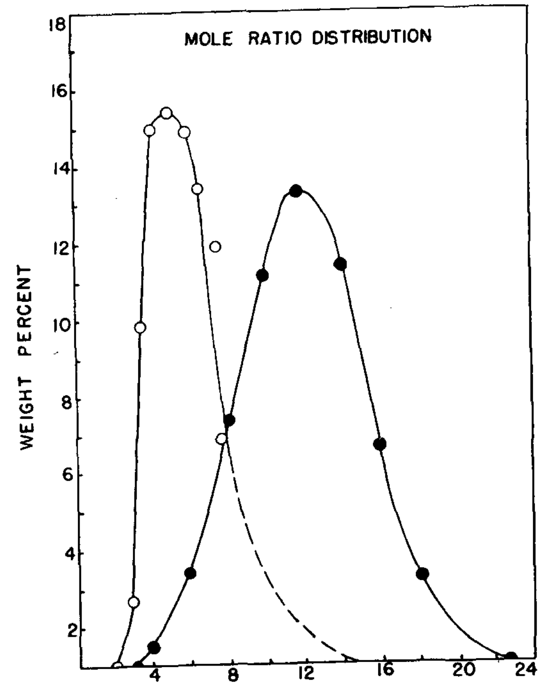


FIG. 1. Mole ratio distribution of ethylene oxide in polyoxyethylated surfactants: ○, nonylphenol plus 6 moles of ethylene oxide; ●, ethylene glycol plus 10 moles of ethylene oxide.

This study (Figure 1) shows that polyoxyethylene glycol containing an average of 10 ethylene oxide units would have 79.6% of the material in the range 8-16. Therefore mole ratio of ethylene oxide to the base material must of necessity be referred to as an average figure. Obviously, the composition represented by Flory's curve in Figure 1 may be altered in two ways and yet give a material having the same average number of moles of ethylene oxide. That is, it may be either narrowed appreciably so that the resulting product contains a relatively high proportion of molecular species close to the average mole ratio, or by increasing the proportion of low molecular weight and high molecular weight species, the curve may be greatly flattened.

In view of this it was decided that it would be of great interest and value to determine to a limited degree not only the mole ratio distribution of some typical polyoxyethylated nonylphenols but also the effect of mole ratio distribution on the physical properties of these compounds. This has been accomplished by molecularly distilling two compounds prepared in the conventional manner with average mole ratios of 6 and 9.5, respectively.

Experimental

The molecular distillation was conducted in a Centrifugal Cyclic Batch Molecular Still (CMS-5; Distillation Products Inc.). In a distillation of this type the batch is first passed over the rotor at room temperature for degassing. The rotor temperature is then set at the lowest desired temperature, the entire batch cycled over the heated rotor, and the distillate removed at a starting pressure of 10 microns. This cycling procedure is repeated at progressively higher temperatures until the working pressure reaches approximately 20 microns. At this point the distillation is stopped. It should be emphasized that all a molecular distillation accomplishes is to narrow the range of mole ratio distribution by decreasing the number of molecular species. It is obvious from Poisson's distribution formula that it is extremely difficult to isolate a single molecular species. However it is possible for research purposes to obtain an extremely narrow distribution range by repeated distillations.

A summary (Table I) of the molecular distillation data on the surfactant with an average mole ratio of six ethylene oxide units indicates that the distillation was discontinued at 280°C., at which point the pressure had reached approximately 20 microns. Although the maximum amount of distillate was obtained in cycle 9, it is evident from the mole ratio of ethylene oxide to nonylphenol (calculated from terminal hydroxyl number determination) that the distillate from cycle 10 most closely resembles the starting material in this respect.

A curve (Figure 1) was plotted on the 6-mole material for percentage of charge distilled versus mole ratio of ethylene oxide. As might be predicted, a curve similar to that for polyoxyethylene glycol (Figure 1) is also obtained for this material. The residue which contains the compounds of higher molecular weights might be expected to fall directly in line if the distillation had been continued in order to separate the higher mole ratios. This was not practical because of the high molecular weights of these species.

The starting material, prepared conventionally, has the property of forming a stable, translucent, colloidal solution in water. Polyoxyethylated nonylphenols with progressively lower mole ratios of ethylene oxide gradually decrease in water solubility so that the lower mole ratio surfactants are completely insoluble. For example, a product formed by the reaction of nonylphenol with four ethylene oxide units is water insoluble but quite soluble in most hydrocarbons. On the other hand, the water solubility of the polyoxyethylated nonylphenols is increased directly as the ethylene oxide chain is lengthened except for an anomaly which will be discussed later.

Considered from a solubility viewpoint, the cloud point data on cycles 9-13 are very informative. Nonionic surfactants of this type exhibit the characteristic generally of being less soluble in hot water than in cold water. This rather unusual phenomenon has been attributed to the fact that association occurs between the neutral ether linkages of the nonionic and the water molecules. This association is partially destroyed on heating, and the material becomes only sparingly soluble. The temperature at which the surfactant is thrown out of solution is referred to as the cloud point. Therefore, to some extent, the cloud point may be taken as a measure of water solubility.

From the cloud point data, distillation cycle 12 with a mole ratio of 7.6 ethylene oxide units is completely soluble in water at room temperature. In the next column showing the cloud points of samples prepared in the conventional manner to correspond to the mole ratios of the distillation products a mole ratio of at least 8.3 ethylene oxide units is nceessary for water solubility at room temperature. These data indicate that the mole ratio distribution curves of the distillation cycles are more peaked than the corresponding curves for the conventional materials. It therefore follows that the range of molecular species

TABLE I

Summary of Distillation Data for Nonylphenol Plus 6 Moles of Ethylene Oxide[a]

Cycle No.	Rotor Temp. °C.	% Charge Distilled	Cloud Point °C.	Cloud Point °C. (Exp. Samples)[b]	Mole Wt.	Mole Ratio of Et. Ox.	Refr. Index (25°C.)
4	100	0.18	......	......	......	......	1.5039
5	120	1.72	......	......	355	3.0	1.5003
6	140	4.62	......	......	356	3.1	1.4980
7	160	8.78	......	......	378	3.6	1.4963
8	180	14.11	......	......	406	4.2	1.4945
9	200	14.41	......	......	445	5.1	1.4930
10	220	13.92	<0	<0	479	5.9	1.4911
11	240	12.37	11	<0	514	6.7	1.4898
12	260	10.91	38.5	0	556	7.6	1.4882
13	280	5.97	50.0	7	559	7.7	1.4878
	Residue	11.48	75.5	31	584	8.3	1.4863
	Trap	0.80	......	......	......	......	......
	Not recovered	0.70	......	......	......	......	......

[a] Refractive index at 25°C., 1.4919; cloud point, cloudy at 0°C.
[b] Samples of same mole ratio prepared conventionally.

TABLE II

Summary of Distillation Data for Nonyl phenol Plus 9.5 moles of Ethylene Oxide[a]

Cycle No.	Rotor Temp. °C.	% Charge Distilled	Cloud Point °C.	Cloud Pt. °C. (Exp. Samples)[b]	Mole Wt.	Mole Ratio of Et Ox.	Refr. Index (25°C.)
2	140	0.17	......	......	......	......	1.4949
3	160	0.87	......	......	343	2.8	1.4949
4	180	2.27	......	......	395	4.0	1.4938
5	200	3.61	......	......	424	4.7	1.4927
6	220	7.27	<0	<0	475	5.8	1.4912
7	240	10.00	10.0	<0	505	6.5	1.4893
8	260	11.92	37.5	13.0	559	7.7	1.4883
9	280	12.42	585.	48.5	609	8.9	1.4873
10	300	12.18	73.0	60.5	644	9.7	1.4858
11	320	10.62	83.0	63.5	691	10.7	1.4850
	Residue	24.68	>100.0	92.5	831	13.5	1.4832
	Trap	1.06	......	......	......	......	......
	Not recovered	2.92	......	......	......	......	......

[a] Refractive index at 25°C., 1.4862; cloud point, 56°C.

[b] Samples of same mole ratio prepared conventionally.

in each cycle is considerably narrowed. For example, cycle 12 is completely soluble at room temperature because most of the low mole ratio compounds which impart water insolubility characteristics to this distillation fraction have been removed by distillation in the previous cyclizations.

A summary (Table II) of the distillation data for the surfactant with an average of 9.5 moles of ethylene oxide units follows the same general pattern as that for the 6-mole material (Table I). However since we are working with a higher average molecular weight compound, the distillation continued to 320° C., at which point the distillation pressure reached 20 microns. It is of interest here also that the distillation fractions are much more hydrophilic as shown by higher cloud points than samples of the same average mole ratio prepared in the conventional manner.

In this distillation, molecular weight determinations show cycle 10 to represent most closely the original material although a greater amount of distillate was removed during cycle 9. This is the same phenomenon which was observed on the distillation of the 6-mole compound.

Curves of refractive indices versus mole ratio of ethylene oxide to alkylphenol have been plotted (Figure 2) for all fractions from both distillations. The upper curve represents surfactants obtained by regular procedures. As might be expected, the distillation fractions follow the same general behavior pattern as the conventional samples although their values are consistently slightly lower. This slight difference is probably due to the loss of impurities from the main batch during the degassing and the early distillation cycles. These data suggest the possibility of using refractive index as a means of production control.

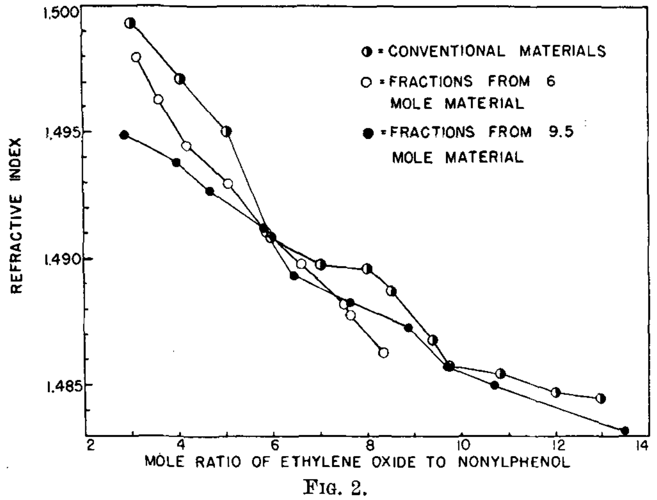


FIG. 2.

Surface tension and interfacial tension on all the distilled fractions from both compounds were measured and compared to values obtained from the starting materials. Only the water-soluble fractions were tested since the water-insoluble fractions tend to gel and settle out in an aqueous medium. No large significant differences were noted at any point. Since no trends were established, work along this line was not extended.

TABLE III

Solubility Data

Surfactant Concentrations—5%

Cycle No.	Mole Ratio of Et. Ox.	Fractions from 9.5 Mol Ratio Material		Conventional Materials[a]	
		Water	Kerosene	Water	Kerosene
3	2.8	I	S	I	S
4	4.0	I	S	I	S
5	4.7	D	S	D	S
6	5.8	D	S	D	S
7	6.5	I	S	D	S(C)
8	7.7	S	I	I	I
9	8.9	S	I	S	I
10	9.7	S	I	S	I
11	10.7	S	I	S	I
Residue	13.5	S	I	S	I

[a] Corresponding to same mole ratio as cycle numbers.

Legend: S = Soluble
S(C) = Soluble, slightly cloudy
D = Dispersible
I = Insoluble

Solubility data (Table 3) compare the solubility in kerosene and water of the molecularly distilled fractions against samples of the same mole ratio compounds prepared conventionally. These data were obtained by mechanically shaking for 30 minutes 5 g. of the surfactant to be tested in 95 g. of solvent. Two definite relationships are established here: a) greater water solubility is obtained with the distilled fractions with a shorter average ethylene oxide chain length as shown in cycle 8, and b) the same is true for slightly greater kerosene solubility as shown in cycle 7. For solubility purposes one might find it profitable in some cases to alter the procedure of manufacture for the polyoxyethylated nonylphenols. In so doing, it may be possible to maintain a definite hydrophobe-hydrophile balance even though the average chain length of ethylene oxide might be varied considerably.

It is of great interest here that cycle 7 (mole ratio of 6.5) is insoluble in water whereas cycles 5 and 6 are dispersible, and cycle 8 is completely soluble. The phenomenon observed with a 10% concentration of cycle 7 in water in a 100-ml. graduate was the formation of multigel-like particles which gradually settled out in one continuous phase to a volume of approximately 43 ml. At this mole ratio of ethylene oxide the surfactant has a hydrophobe-hydrophile balance which is on the brink of complete water solubility. The same system occurs with the conventional samples except that, as might be predicted, the phenomenon occurs at a higher average ratio of ethylene oxide (i.e. 7.7 moles). Again the compound directly above it is completely dispersible in water, but the compound below, with an average mole ratio of 8.9, is completely water soluble.

These data will now be correlated with a similar anomaly observed in the wetting efficiency of the undistilled fractions, in which a large decrease in wetting is found at this insoluble point.

Wetting data collected on the various cycles are both interesting and informative.

The relative wetting capacities of cycles 5 through 11, as well as the residue of the 9.5 mole material, were run according to the standard Draves-Clarkson test, using 5-g. cotton skeins, a temperature of 25°C., a 3-g. hook, and a 25-second wetting-out time (5). For comparison data, the wetting data for the distilled fractions from the 6.0 and 9.5 materials and for the conventional materials has been plotted against the percentage of the undistilled 9.5-mole product as a standard (Figure 3). These curves are unusual in that there is an unexpected drop in wetting capacity in each case. This is contrary to the generalizations which have been made by Sisley and others (1. 2) concerning the effect of mole ratio on wetting capacity. It is generally stated that the wetting capacity of a polyoxyethylated nonionic increases with increased mole ratio of ethylene oxide until a maximum has been reached, after which there is again a decrease in wetting ability of the nonionic surfactant. Actually, however, this is not the case with the polyoxyethylated nonylphenols. There are actually two peaks in each curve which shows that this phenomenon is observed also with the conventional materials although the minimum point is displaced somewhat to the right. The minimum point for cycle 7 (mole ratio—6.5) may be correlated with its unexpected insolubility in aqueous solution (Table 3) since it exhibits the astonishing and paradoxical property of forming an apparent hydrate and then becoming water-insoluble when further dilution is attempted.

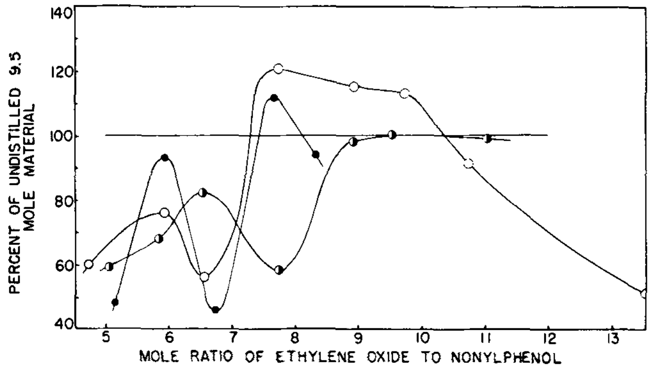


FIG. 3. Wetting capacity of distilled fractions compared to the undistilled 9.5-mole material: ○, fractions from 9.5-mole material; ●, fractions from 6.0-mole material; ◑, surfactants prepared conventionally with normal mole ratio distribution curves.

The fact that it is possible to obtain wettings as high as 120% of standard is very impressive in view of the fact that the undistilled material is *per se* a very effective wetting agent. This surfactant gives a 25-second wetting-out concentration of 0.4 gram/liter, using the Draves-Clarkson test (5). In an application involving wetting as a desirable physical property one might find it profitable to investigate the possibility of improving the performance of a nonionic surfactant by producing a material similar to that obtained by molecular distillation.

Nonionics of the polyoxyethylated alkylphenol type find numerous applications as emulsifiers in the formulations of insecticides, herbicides, sanitary chemicals, pharmaceuticals, cosmetics, textile auxiliaries, metal cleaners, and various other industrial emulsions. Therefore the fractions from both the distilled surfactants were tested in emulsion formulations and compared to the undistilled material. In this way it was believed that it might be possible a) to determine whether a delicate hydrophobe-hydrophile balance is needed in emulsification, and b) to help verify some previous experimental evidence which indicated that in some instances a large variety of molecular species is more desirable.

The emulsifying capacity of the distilled fractions of the 6-mole material has been compared to the undistilled material in toxaphene formulations. In each test, the formulation contained 45% toxaphene, 47% kerosene, and 8% emulsifier. The spontaneity of emulsification was tested by adding 2 ml. of the formulation to 98 ml. of 342 p.p.m. hard water from a pipette held approximately 4 cm. above the water surface. For purposes of this test hard water is defined as water designed to give a total hardness of 342 p.p.m., calculated as calcium carbonate: calcium chloride, an-

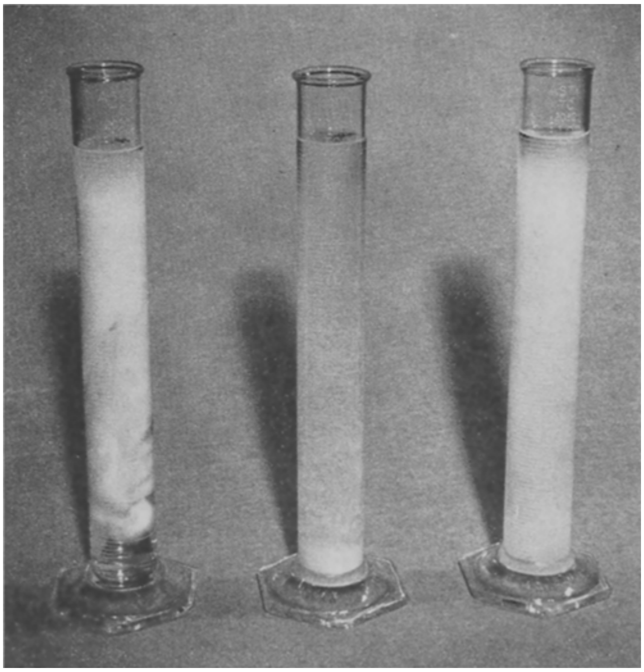


FIG. 4. Emulsifying capacity of distilled fractions from 6-mole material in toxaphene formulations: left, undistilled 6-mole material, center, cycle 10; right, cycle 12.

hydrous—0.3037 g., magnesium chloride hexahydrate—0.1388 g., distilled water to make one liter.

A photograph (Figure 4) was taken to compare the spontaneity of emulsification of formulations containing the undistilled surfactant, cycle 10 which has the same mole ratio as the base material, and cycle 12 which gave the best emulsion from the distilled fractions. One can easily observe the distinctly superior "bloom" exhibited by the formulation containing the undistilled material. The emulsion prepared with the undistilled material also gave the best 24-hour stability.

The undistilled 9.5-mole surfactant has been found to be a good emulsifier for DDT dissolved in a hydrocarbon solvent. The distillation fractions of this surfactant were therefore tested for their emulsification capacity in a test mixture composed of 25% DDT, 72% xylene, and 3% emulsifier. The emulsions were prepared with 20 cc. of formula and 80 cc. of 342 p.p.m. water. The mixtures were inverted twice manually and the system allowed to come to equilibrium.

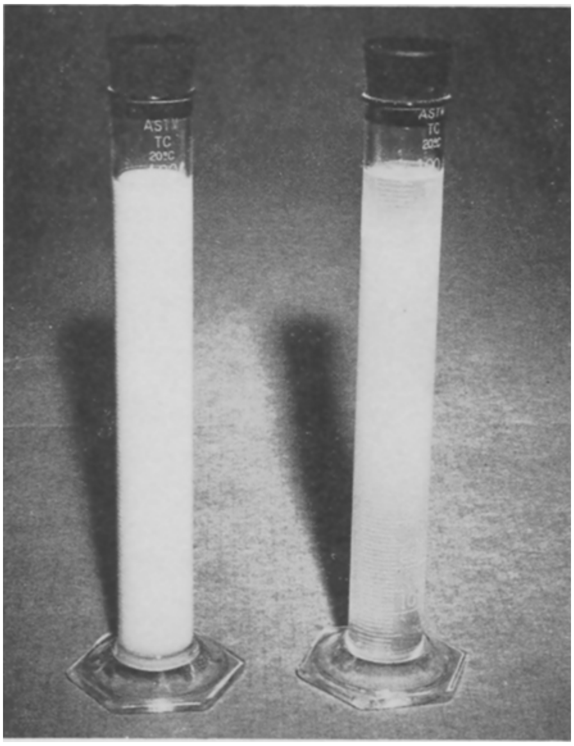


Fig. 5. Emulsifying capacity of distilled fractions from 9.5-mole material in DDT formulations: left, undistilled 9.5-mole material; right, cycle 11 from the distilled fractions.

Figure 5 clearly illustrates the superiority for the regular 9.5-mole material. As can be readily seen, the emulsion on the left is much more opaque and has creamed without oil actually separating while the emulsion containing the distilled product has oiled badly and very little emulsification has occurred. These results demonstrate the fact that a rather wide range of molecular species is desired in general for emulsification and that there is nothing to be gained from an emulsification standpoint by narrowing the mole ratio distribution.

Another important characteristic of surfactants is their ability to produce foam, especially in aqueous medium. The foam-producing capacity of the distilled fractions 5 through 11 from the 9.5-mole material was compared to undistilled conventionally prepared surfactants of the same mole ratios as the distilled fractions using the Ross-Miles test (6). These data bear out a fact fairly well recognized that water solubility is a prime prerequisite for foaming for nonionic surfactants. As can be readily seen (Figure 6), the best initial foam from the fractions was obtained with water soluble cycles 8, 9, 10, and 11. However the undistilled product curve has a much steeper slope so that at approximately 10.6 moles the two curves coincide. No appreciable difference was noted in foam stability of the two materials. Foam stability may be defined as the foam volume remaining after definite periods of time (6). Thus foam stability is differentiated from initial foam volume.

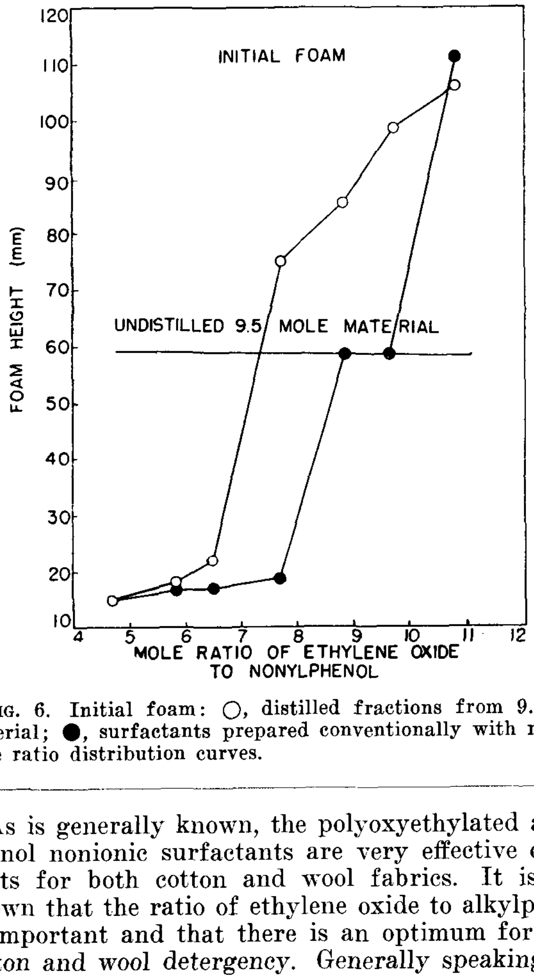


Fig. 6. Initial foam: ○, distilled fractions from 9.5-mole material; ●, surfactants prepared conventionally with normal mole ratio distribution curves.

As is generally known, the polyoxyethylated alkylphenol nonionic surfactants are very effective detergents for both cotton and wool fabrics. It is also known that the ratio of ethylene oxide to alkylphenol is important and that there is an optimum for both cotton and wool detergency. Generally speaking, detergency is not as sensitive to changes in hydrophobe-hydrophile balance as is wetting. However no data were available concerning the effect of mole ratio distribution on cotton and wool detergency.

In view of this the distilled fractions from the 9.5-mole surfactant were tested for both cotton and wool detergency. At the same time their detersive performance was compared to the conventional 9.5-mole material.

For cotton detergency testing, broadcloth swatches were soiled with a synthetic soil described by Lambert and Sanders (7) to an initial reflectance (Reflectometer) of approximately 30, using a magnesium oxide block as a reference. Employing a U. S. Testing Co. Terg-o-tometer, the swatches were washed in distilled

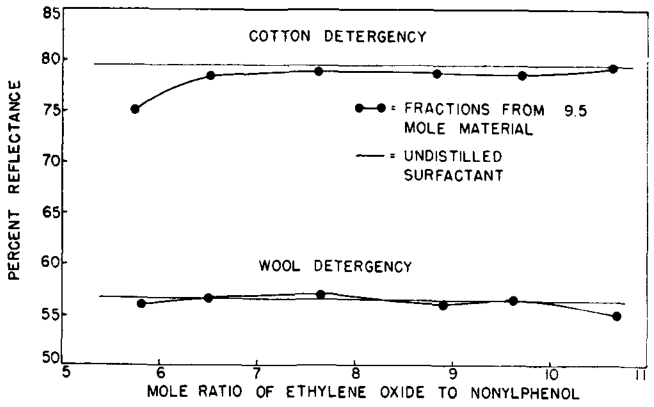


FIG. 7.

water containing 2.5 g. per liter of surfactant at 60° C. for 15 minutes. They were rinsed in the Terg-o-tometer in distilled water for two minutes and then dried in a hot-air oven at 50°C.

The wool swatches were soiled from a carbon tetrachloride suspension of carbon black and mineral oil to a reflectance also of approximately 40. These were also washed in the Terg-o-tometer, using distilled water which contained 2.5 g. per liter of surfactant.

The results (Figure 7) show that there is no significant difference between distilled and undistilled products with respect to both cotton and wool detergency.

Summary

It has been shown repeatedly (1, 2, 3) that for polyoxyethylated nonionic surfactants a certain hydrophobe-hydrophile balance (i.e., average mole ratio of ethylene oxide to hydrophobic material) is necessary to obtain maximum wetting, optimum detergency, etc. A study has been conducted to determine the effect of mole ratio distribution of ethylene oxide on the physical properties of a polyoxyethylated nonylphenol. This was accomplished by molecularly distilling two nonionics: a nonylphenol plus 6.0 moles of ethylene oxide and a nonylphenol plus 9.5 moles of ethylene oxide. The following conclusions have been reached concerning the effect of mole-ratio distribution on the physical properties of these surfactants.

1. The mole ratio distribution of ethylene oxide in a polyoxyethylated nonylphenol follows the Poisson formula and curve in a manner analogous to the polyoxyethylene glycols (Fig. 1).
2. The hydrophobe-hydrophile balance of the undistilled surfactant may be altered by molecular distillation. This is accomplished by narrowing the range of molecular species.
3. Wetting which is superior to the undistilled material may be effected by narrowing the distribution of molecular species (Figure 3).
4. Fractions from the distilled surfactant showed slight improvement in initial foam volume at certain mole ratios of ethylene oxide to base material over the undistilled material (Figure 6). No change in foam stability was noted.
5. Although there is an optimum ratio of ethylene oxide to the hydrophobic base at which maximum cotton or wool detergency is obtained, cotton and wool detergency are relatively unaffected by mole ratio distribution (Figure 7).
6. Surface and interfacial tension are also comparatively unaffected by mole ratio distribution change.
7. Emulsifying properties of these materials are adversely affected by narrowing the mole ratio distribution.

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Industrial Fat Splitting

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UNTIL quite recently fat hydrolysis had been considered as a heterogeneous reaction that occurs in the oil-water interface (3, 4, 10, 16). However Lascaray has shown (6, 7, 8, 9) that in the industrial Twitchell and autoclave splitting processes this reaction is essentially homogeneous and takes place in the oil phase, thanks to the dissolution of small quantities of water in it, continually renewed by stirring of the phases.

Later on Suen and Chien (15) deduced from their experiments by the sulfuric acid method that acid hydrolysis also occurs in the oil phase, being a reaction of the first order with respect to the unhydrolyzed oil. Mills (11) considers it obvious that the reaction takes place in the oil phase. Sturzenegger and Sturm (14), in a study of hydrolysis at high temperatures, agree with Lascaray's theory. Hartmann (2), on studying the kinetic order of splitting by the Twitchell process, reaches the conclusion that the resulting first-order reaction can be accounted for in the simplest way by assuming that the hydrolysis takes place in the oil phase. Bailey (1) considers the Lascaray theory today as generally admitted. Finally, Yanase (17) confirms the small importance of the heterogeneous reaction in Twitchell splitting by demonstrating that the addition of emulsifying agents gave no particular benefit.

It thus appears that the main works of investigation on fat hydrolysis published in the last 10 years agree upon a homogeneous hydrolysis in the oil phase and that this theory is of general value since it is applicable with the same efficacy to the different industrial splitting processes, whether autoclave, Twitchell, high pressure, or sulfuric acid methods.

Therefore it seems desirable to review, under this new aspect, the different phases of the industrial fat splitting and to try to establish rules of general application.