

NONIONIC DETERGENTS

J. V. KARABINOS AND MAX C. METZIGER

Blockson Chemical Company, Joliet

INTRODUCTION

The term detergent in the broad sense applies to almost any type of cleaning agent. However, more specifically the term usually implies the use of synthetic substitutes for soaps. The first detergent introduced into this country in the early 1930's was "Dreft", and since then many other sulfates ($R-O-SO_3Na$) or sulfonates ($R-C_6H_4-SO_3Na$) have been developed; at the present time the sale of detergents exceeds that of soaps. These sulfated and sulfonated products are usually referred to as the anionic type since the hydrophobic group possesses a negative charge. Another class of detergents, where the hydrophobic groups are positively charged, has received less attention, possibly for economic reasons and because of their limited use in acidic solutions. These detergents are referred to as the cationic type ($R-N(R')_2H^+ Cl^-$) and possess a quaternary ammonium structure with at least one long chain aliphatic R group. The principle advantage of the cationic detergents is their bactericidal activity.

Schoeller and Wittwer (1934) were granted a U.S. patent on textile detergents wherein the hydrophobic group R is still a long chain aliphatic alcohol or acid, but the hydrophilic group consists of a polymerized ethenoxy chain of sufficient length to make the fatty

group soluble in water. Since no ionic linkages are involved, these substances have been referred to as nonionic ($R-O-(CH_2-CH_2-O)_n-H$) detergents. Following the Second World War these detergents were successfully introduced and marketed in this country for automatic laundering and dishwashing machines. One of the main reasons for the growing market for these substances is their tendency to produce low-foam, sometimes referred to as "controlled sudsing", which is desirable in automatic equipment, and their excellent cleaning properties, particularly when admixed with alkaline builders such as polyphosphates, silicates, carbonates, etc. (See Metziger and Karabinos (1956) for a review of these builders). Since very hard water, such as is found in most of Illinois, produces a detrimental effect due to the precipitation of calcium and magnesium salts of anionic detergents and soaps, the nonionic polyoxyethylene detergents would be more desirable since one would expect them to be much less affected by these factors. This paper includes some general information on this group of detergents, as well as a description of recent experiments carried out in this laboratory.

NONIONIC DETERGENTS OF INDUSTRIAL IMPORTANCE

Tall Oil.—Polyoxyethylene esters produced from tall oil, a fatty acid-

rosin acid mixture obtained from the pine wood paper pulp industry, represent the largest fraction of nonionics being manufactured at the present time. The main reason for their usage is the relative low-cost of this hydrophobic base, as well as the excellent detergent properties of the resultant mixture. The fatty acids (50-70%) of tall oil consist mainly of oleic and linoleic acids, and the rosin acids (30-50%) are comprised of a half-dozen or more acids related to abietic (Ball and Vardell, 1951:137). The hydrophobic group in most of the nonionics is usually condensed with ethylene oxide, under low pressure and in the presence of an alkaline catalyst such as potassium carbonate or hydroxide, until the length of the polymerized chain is sufficient to solubilize the fatty portion of the molecule. Detergency studies with tall oil with respect to ethenoxy chain length (Stoltz, *et al.*, 1953:271) as well as with fatty alcohols (Karabinos, *et al.*, 1954:419), fatty acids (Ballun, *et al.* 1954:20), and a sistosterol mixture (Karabinos and Ballun, 1954b:136) have been carried out and indicate that for each carbon atom in the hydrophobic portion of the molecule approximately two-thirds of an ethylene oxide unit is required for complete solubility and optimum detergency. For example, approximately 13 ethenoxy units are required for tall oil which averages about 19-20 carbon atoms. Another way of expressing this relationship is that one part by weight of hydrophobe requires two parts of ethylene oxide. Further addition of ethylene oxide has no beneficial effect upon detergency and in some cases, particularly with hydrophobic groups

of lower molecular weight, an adverse effect was noted, probably as a result of dilution. Substitution of the groupings, either on the alcoholic end group or on the hydrophobic part of the molecule, did not enhance detergency (Kapella *et al.*, 1954:392) and in some cases substitution proved to be deleterious. The analyses of tall oil nonionics with relation to ethenoxy content were carefully studied (Ballun *et al.*, 1955:81) as was the correlation of physical properties such as surface tension, density, refractive index, etc. with ethenoxy chain length (Cronin *et al.*, 1955:196). The ethenoxy chain length of the tall oil nonionics can also be determined by a cloud point method or by the Rast molecular weight determination using camphor (Karabinos *et al.*, 1955:49). Knowing the nature of the hydrophobic group is always helpful. From this standpoint it seems worthwhile to mention that a tall oil nonionic can be differentiated from other nonionics as well as from the anionic detergents using a series of qualitative tests (Karabinos *et al.*, 1954:41). The main tall oil nonionics manufactured today are "Sterox CD" (Monsanto), "Renex 20" (Atlas) and "Teox 120" (Blockson). For actual detergent usage these products are usually blended with the aforementioned alkaline builders (Harris, 1951; Harris and Kosmin, 1951) to produce saleable powders. For example, Monsanto's "All" is rapidly expanding into the automatic washing machine field, and many other similar products are sold under a large variety of local trade names. It might also be mentioned that tall oil-ethylene oxide condensates are

quite dark in color and decolorization can be accomplished by addition of ozone or hydrogen peroxide (Karabinos and Ballun, 1954a:71).

Alkyl Phenol.—Diisobutylene or tripropylene from the petroleum industry is condensed in a Friedel-Crafts reaction to produce the isomeric octyl or nonylphenols, respectively. These phenolic hydrophobic groups are treated with ethylene oxide in a manner similar to that used for tall oil, and the polyoxyethylene alkylphenates produced represent another large group of nonionic detergents. When admixed with alkaline builders these substances likewise produce excellent detergent mixes (Harris, 1950). However, the higher cost of producing alkylphenols prevents them from being competitive with the tall oil nonionics. Some of the common alkylphenol based nonionics are sold under the trade names of "Igepal" (Antara), "Oronite Dispersant" (Oronite) and "Triton" (Rohm and Haas) and are employed in textile processing as well as in specialties.

Fatty Acids and Alcohols.—A number of fatty acids such as stearic and oleic, as well as fatty alcohols derived from these acids, are marketed by a variety of companies. Those with a lower ethylene oxide content are sold as emulsifiers for fats, and the water soluble products could find use in detergent mixtures if the price of fatty acids becomes competitive. This is a distinct possibility since the price of tallow has been dropping steadily. One product of recent interest is the primary tridecyl alcohol obtained from the oxo-process using the petroleum industry's tetrapropylene. This latter hydrophobe likewise forms a

polyoxyethylene ether of considerable interest, particularly in the higher-foaming, liquid, hand-dishwashing compositions.

Thioethers.—Recently the tertiary dodecyl mercaptans have become available, presumably from the above mentioned tetrapropylene. Condensation of the mercaptan with ethylene oxide likewise produces a polyoxyethylene dodecyl thioether (Durgin, 1952). Some of the more common thioethers are known under the trade names "Nonic" (Sharples) and "Sterox SK" (Montanto). They are recommended for textile processing and in dishwashing compositions. However, one drawback seems to be the instability of the thioether linkage to oxidizing agents.

Propylene Oxide.—A very interesting group of nonionic detergents are the "Pluronics" manufactured by the Wyandotte Corp. (Vaughn *et al.*, 1952:240). A hydrophobic polyoxypropylene glycol is made by polymerizing propylene oxide and this is condensed with ethylene oxide. The "Pluronics" are recommended for dishwashing compounds, textile soaping-off prints and in dye levelling.

One of the advantages of these substances is that they can be produced as a free-flowing powder which is more easily mixed with inorganic constituents than are viscous oils. However, as with some of the other nonionics, the cost of this detergent is not competitive for general usage.

Miscellaneous.—A number of modifications of nonionic detergents have also been marketed. For example, a fatty acid such as stearic is esterified with sorbitan, an an-

hydride of sorbitol, and the resultant product is condensed with ethylene oxide to form a polyoxyethylene sorbitan monostearate. These substances known as the "Tweens" (Atlas) are mainly used as emulsifiers, particularly in the food industry. Similar derivatives, *e.g.* polyoxyethylene sorbitol laurate known as "Atlox" and a polyoxyethylene sorbitol-beeswax, are also marketed by the same firm. The former is used in formulating agricultural chemicals and the latter is recommended as an emulsifier for cosmetics.

In some instances a smaller quantity of ethylene oxide is condensed, for example with an alkylphenol, and the alcohol group is esterified with sulfuric acid to form a polyoxy-

ethylene alkylphenol sulfate. One such product is known as "Alipal" (Antara), and although this substance is essentially an anionic detergent it is mentioned here to show the type of modifications which can be made with nonionic detergents. The sulfated derivatives produce much higher foaming and hence are useful in hand dishwashing and in shampoos.

HYDRATION OF NONIONIC DETERGENTS

From polarimetric studies (Karabinos, Hazdra and Ballun, 1955) in this laboratory, it appears quite likely that the nonionic detergents exist in a hydrated state in aqueous solution; furthermore, it also appears that the detergent properties of

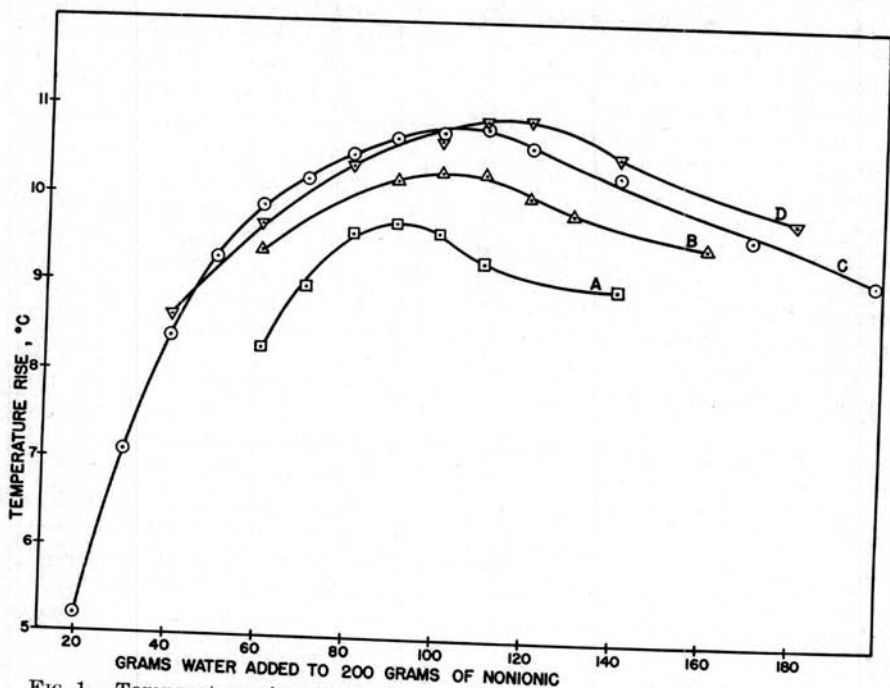


Fig. 1.—Temperature rise obtained upon addition of water to several nonionics: A, tall oil ester (8.6 ETO); B, nonylphenol ether (11.0); C, tall oil ester (12.4); D, tall oil ester (17.1).

these substances are largely due to the presence of water molecules. For example, detergency experiments in non-aqueous solutions or where the hydration has been suppressed (Karabinos, Kapella, Ferlin and Sawhill, 1955) strongly indicate the necessity of this hydration for detergency. Nonionics undergo interesting viscosity changes (Karabinos and Ballun, 1955) when admixed with water, and the changes seem to depend largely on the nature of the hydrophobic group rather than on the ethenoxy chain length.

HEAT OF HYDRATION EXPERIMENTS

When water is added to the ethylene oxide nonionics, a considerable amount of heat, apparently due to hydration, is given off. If one assumes that a maximum temperature rise would be obtained when an optimum quantity of water, representing stoichiometric proportions, has been added to the polyglycol, one may infer that these proportions represent the formation of a definite hydrate. With this in mind, 200-gram portions of several ether and ester nonionics were diluted with varying amounts of distilled water, and rises in temperature were accurately measured with a calorimeter. The temperatures of both

the water and the nonionic were adjusted to 28°C before addition, and the maximum temperature after dilution was recorded, usually after several minutes. The difference between the initial and final temperatures (heat rise) upon dilution is illustrated in Figure 1 for several nonionics from tall oil containing 8.6 (A), 12.4 (C), and 17.1 (D) mols of ethylene oxide, respectively, as well as a nonionic from nonylphenol (B) containing 11 ethenoxy units. (The preparation and determination of the chain length of the tall oil nonionics is described in another article, Ballun *et al.*, 1955:81). It would thus appear that a maximum temperature rise is obtained in each case and the optimum amount of water indicated in Figure 1 combining with 200 gms. of nonionic is shown in Table 1 in comparison with the theoretical amount of water necessary to hydrate each nonionic to the extent of two molecules of water for each oxygen atom in the hydrophilic chain.

From this experiment it would appear that at least two molecules of water are combined in some type of hydrate formation with each ethylene oxide unit. This water of hydration or association then becomes an integral part of the non-

TABLE 1.—Heat Rise Upon Addition of Water to Nonionics.

Designation from Fig. 1	Hydrophobe	Ave. no. ethenoxy units	Mol. wt.	Grams water/200 gms. nonionic	
				Theory for 2 H ₂ O/oxygen	Obtained from max. heat rise (Fig. 1)
A.....	tall oil.....	8.6	668	92.5	90
B.....	nonylphenol	11.0	704	112	110
C.....	tall oil.....	12.4	836	107	110
D.....	tall oil.....	17.1	1043	118	120

ionic molecule in aqueous solution. The concept of solvation of nonionics is not new, since it has been surmised on the basis of inverse solubility, *i.e.* decreasing solubility of polyoxyethylene glycol ethers and esters with rise in temperature of their aqueous solutions. However, the extent of solvation in concentrated aqueous solution seems to be indicated by the heat of hydration experiment.

Viscosity and turbidity studies in dilute solutions of a polyoxyethylene alkylphenol indicate that hydrated spherical micelle is formed, consisting of about 140 detergent molecules oriented radially and entrapping some 6000 molecules of water or about 4 water molecules for each oxygen atom (Kushner and Hubbard, 1954:1163). This is not inconsistent with the above studies carried out in concentrated detergent solutions.

STRUCTURE OF NONIONICS IN AQUEOUS SOLUTION

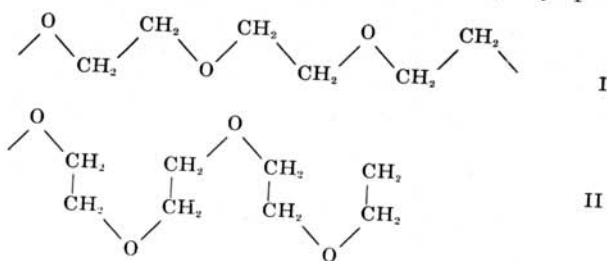
From previous viscosity and X-ray studies (Curme and Johnston, 1952:180) on polyethylene glycols it was well established that the lower polymers exist in a "zig-zag" form (I) while the higher polymers possess a "meandering" form (II).

By analogy these formulae undoubtedly apply to the polyglycol

esters and ethers, except that in aqueous solution the following type of hydrate ($H_2O = (+ -)$) exists probably in both "zig-zag" (III) and "meandering" (IV) forms.

Thus, it would seem the hydrophobic unit is solubilized not so much by the polyglycol chain itself as by the hydrated hydrophilic group. Furthermore, the hydrophilic group quite possibly attains a somewhat *negative character due to the ring of hydrate groups*. To be sure, the hydrophilic group would not be as negatively charged as, for example, the sulfate group of an anionic, but the hydrated polyglycol possibly behaves as a very weak anionic in solution, if not of itself then by virtue of a micellar structure. Experiments with a polyoxyethylene alkylaryl ether (Fine-man and Kline, 1953:288) in 0.1 - 1% aqueous solution indicated that charged metals exhibited rapid soil removal from the cathode and no removal from the anode, thus indicating some ionic character for the nonionic. Similar results were noted with a charged fiber such as nylon by altering the pH.

However, it should be noted that the polyglycols, like the anionic detergent, also possess micelle structure in dilute solution. Cryoscopic evidence (Gonick and McBain, 1947: 334) with an alkylaryl polyethylene



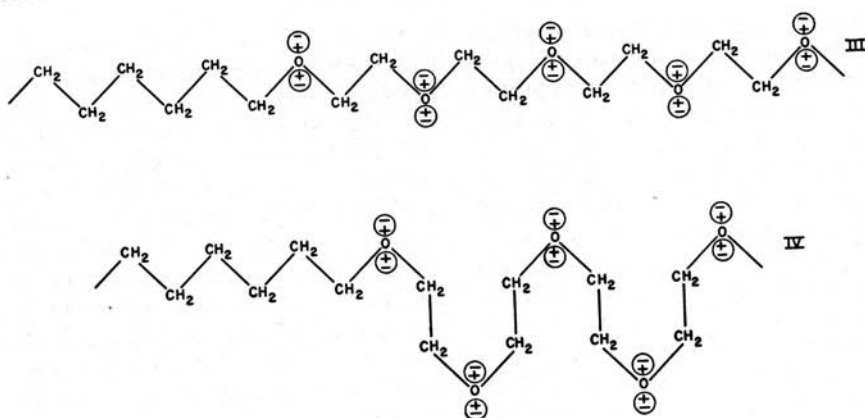


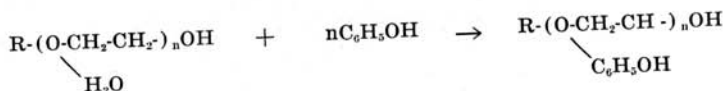
FIG. 2.—Hydrated nonionics.

oxide and nonaethylene glycol monolaurate, as well as viscosity and other experiments (Goto *et al.*, 1954:73) with fatty alcohol polyglycol ethers, suggested that nonionic detergents, like anionic, are characterized by micelle formation, a "critical concentration" for the formation of micelles and expansion of the micelle structure with dilution. X-ray diffraction patterns (Curme and Johnston, 1952:180) also indicated similarity of the nonionic micelles to those of colloidal electrolytes. That water was necessary for micelle formation of pure fatty alcohol polyglycol ethers was demonstrated by X-ray data (Schulman *et al.*, 1951:117). Petroleum ether solutions of the detergents showed no main X-ray diffraction spacing even in high concentrations, but addition of water immediately produced viscous birefringent systems with comparatively sharp X-ray bands. A system with a single surface-active component gave evi-

dence of an ordered lamellar structure that became heterogeneous if the molar ratio of water to ethylene oxide units exceeded 1:1. Systems containing mixed components, as do most of our common nonionic detergents, showed disorder corresponding to the following proposed transitions: lamellae→cylinders→spheres.

BEHAVIOR OF NONIONICS WITH PHENOLS

Earlier investigators (Weiden and Norton, 1953:606; and Livingston, 1954:365) have noted that nonionics may be "salted-out" from aqueous solution by addition of phenol and that some kind of insoluble complex is formed. This information has been applied to the determination of the polyoxyethylene chain length of nonionics (Karabinos, 1955:50), particularly where the nature of the hydrophobic group is known. Presumably the hydrated water molecules of a nonionic are replaced by phenol.



Determinations of freezing points of various compositions of nonionics with phenol have been carried out in this laboratory by A. T. Ballun. Eutectics of nonionics with several dihydric phenols were carried out by Lillian Barnas and Paula Montalto at the College of St. Francis.

The freezing points of various compositions of nonionics with phenol were measured by melting the anhydrous detergent with phenol and following the rate of cooling, *i.e.* the time-temperature curves at

each composition using an evacuated Dewar and a dry-ice acetone bath. These curves were analyzed, and the melting points obtained at each composition when plotted showed eutectic formation between the phenols and nonionics. These curves are illustrated on Figure 3.

The polyoxyethylene nonionics were prepared according to the directions previously published (Karabinos *et al.*, 1954:419). It should be noted that in Figure 3 and in Table 2 the octadecyl ether (6.5) refers to

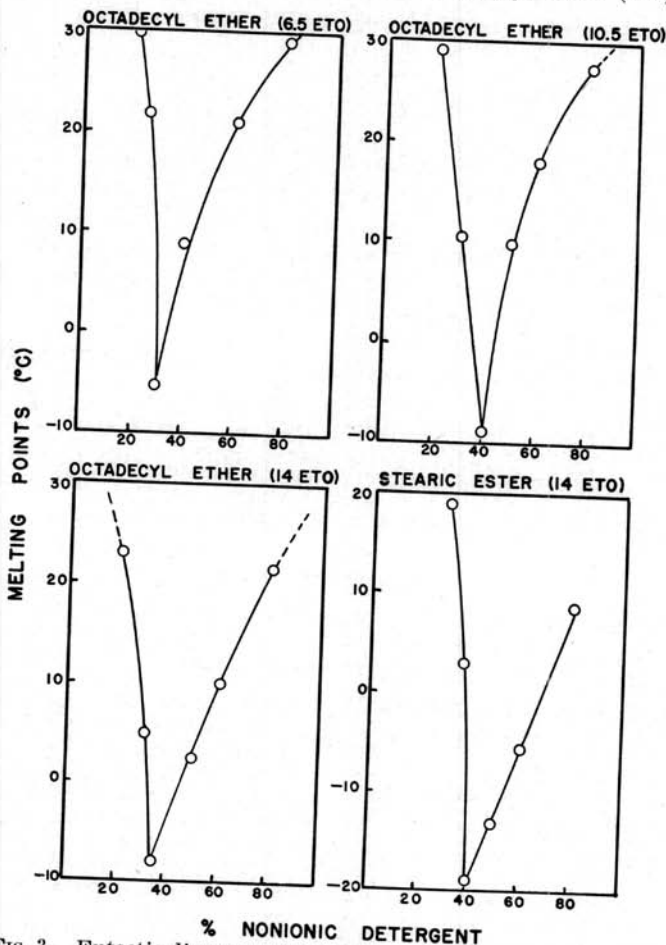


FIG. 3.—Eutectic diagrams of several nonionics with phenol.

TABLE 3.—Eutectic Formation of Nonionic Detergents with Phenol.

	Number ethenoxy units	Composition eutectic point		Moles phenol per mole nonionic	Moles phenol per ethenoxy group
		% phenol	% nonionic		
Octadecyl ether...	(6.5)	70	30	13.7	2.1
Octadecyl ether...	(10.4)	60	40	11.6	1.1
Octadecyl ether...	(14.1)	63	37	17.9	1.3
Stearic ester.....	(14.0)	60	40	14.4	1.0

a polyoxyethylene nonionic wherein 6.5 moles of ethylene oxide was condensed with 1 mole of octadecyl alcohol. The number of moles of ethylene oxide probably represents an average number according to previously published work on the polyglycols themselves (see Curme and Johnston, 1952:180).

From the data shown in Figure 3, it would seem that when nonionics are mixed with phenol, eutectic mixtures are formed at compositions corresponding to either one or two moles of phenol for each ethenoxy unit depending on the ethenoxy chain length. These data are summarized in Table 3.

From these four experiments, one

may speculate that where the ethenoxy chain is short (6.5 ethylene oxide units) and the product is not water soluble, two moles of phenol combine with each oxygen to form a eutectic point. With the remaining three products, where the nonionic is water soluble, approximately one mole of phenol combines with each oxygen atom. However, it would be premature to generalize without further data.

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