

Triton® X Surfactants

Molecular Formula: C₃₃H₆₀O_{10.5}

Molecular Weight: 624 avg

CAS # : 9002-93-1

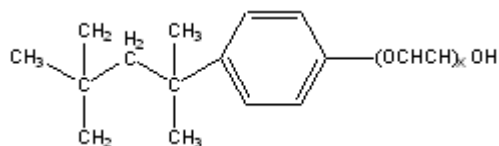
Synonym: Alkylphenol hydroxypolyethylene

Physical Description: Clear colorless viscous liquid

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Introduction

The Triton® X-Series of nonionic surfactants are prepared by the reaction of octylphenol with ethylene oxide. The products are of the type commonly described as alkylaryl polyether alcohols and have the following general structural formula:



in which x indicates the average number of ethylene oxide units in the ether side chain. The series carried by MP consists of the following products, listed in order of increasing length of the polyoxyethylene chain:

Octylphenol Series:

| | |
|---------------------------|----------|
| Triton X-114 | x = 7-8 |
| Triton X-100 | x = 9-10 |
| Triton X-405 (70% active) | x = 40 |

The products are mixtures, with respect to length of the polyoxyethylene chain; the "x" values given above represent the average number of ethylene oxide units in the ether side chain of each product. The distribution of various polyoxyethylene chain lengths in each of the surfactants follows the Poisson distribution.

The principal uses of these surfactants are in industrial and household detergent applications and in

emulsifying agents. They are employed in almost every type of liquid, paste, and powdered cleaning compound, ranging from heavy-duty industrial products to gentle detergents for fine fabrics. These surfactants are also important ingredients of primary emulsifier mixtures used in the manufacture of emulsion polymers, stabilizers in latex polymers, and emulsifiers for agricultural emulsion concentrates, and wettable powders.

Typical Physical Properties

| | Triton® Nonionic Surfactant | | |
|---|-----------------------------|------------|------------------|
| Property | X-114 | X-100 | X-405 (70%) |
| Form | Liquid | Liquid | Aqueous Solution |
| Average EO Units | 7-8 | 9-10 | 40 |
| Active Ingredient, % | 100% | 100% | 70% |
| Color, APHA | 100 | 100 | 250 |
| Specific Gravity, 25°/25°C | 1.054 g/ml | 1.065 g/ml | 1.102 g/ml |
| Density, lb/gal | 8.8 | 8.9 | 9.2 |
| Viscosity, Brookfield ⁽¹⁾ , at 25°C, cP | 260 | 240 | 490 |
| Pour Point ⁽³⁾ , °F | 15 | 45 | 25 |
| Flash Point, Tag Open Cup, °F | > 300 | > 300 | > 212 |
| Cloud Point, 1% aqueous solution, °C | 22 | 65 | > 100 |
| HLB Value (calculated) ⁽⁴⁾ | 12.4 | 13.5 | 17.9 |
| Surface Area ⁽⁵⁾ , Angstrom ⁽²⁾ | 50 | 48-54 | 88 |
| Critical Micelle Concentration (CMC) | 0.2 mM | 0.24 mM | -- |
| Aggregation Number | -- | 140 | -- |

(1) Spindle #2 at 12 rpm

(2) Spindle #2 at 30 rpm

(3) ASTM D 97-57

(4) HLB (Hydrophile-Lipophile Balance values range from 0 (completely lipophilic or oil-loving) to 20 (completely hydrophilic or water-loving) and are calculated by dividing the weight percent of ethylene in the surfactant by 5.

(5) Surface area is the area per molecule in square Angstroms.

Critical Micelle Concentration (CMC): Detergents with high CMC values are generally easy to remove by dilution; detergents with low CMC values are advantageous for separations on the basis of molecular weight. As a general rule, detergents should be used at their CMC and at a detergent-to-protein weight ratio of approximately ten. ⁶⁻⁷

Solubility

The water solubility and surface activity of nonionic surfactants are dependent on the hydrophilic nature of the ether linkages in the polyoxyethylene chain. These ether linkages are readily hydrated at room temperature, and the water solubility of the products at room temperature is dependent on the number of such hydrated ether linkages. The products are listed in the above physical properties table in the order of increasing solubility in water.

In the OPE series, Triton® X-114 and products of longer polyoxyethylene chain length are soluble in water at room temperature.

An increase in temperature reduces the forces of hydration, and the surfactants then become less soluble in water. The nonionics, therefore, normally exhibit a "cloud point," which is the temperature above which all but very dilute aqueous solutions become turbid and eventually form two phases. The cloud point temperature, which is shown for the individual products in the typical properties table, increases with increasing polyoxyethylene chain length in a given series and eventually reaches a value above the atmospheric boiling point of water.

The effect of dissolved inorganic salts on the water solubility of the surfactants is similar to that of increasing temperatures. Most dissolved salts have greater affinity for water than do the ether linkages in the nonionics, and, therefore, the salts essentially dehydrate the nonionics. In the table which follows, the cloud point of Triton® X-100 was determined at a one-percent active ingredient level in various concentrations of sodium hydroxide and deionized water. Unlike anionics, nonionic surfactants do not form insoluble salts in hard water. They are also compatible with solutions of either anionic or cationic surfactants.

Cloud Point of Alkaline Solutions of Triton® X-100 ⁽¹⁾

| | Cloud Point, °C | | | |
|---------------|------------------------|----|----|----|
| | Sodium Hydroxide, wt % | | | |
| | 0 | 1 | 3 | 5 |
| Triton® X-100 | 65 | 57 | 41 | 27 |

(1) 1.0% surfactant, as-supplied, in deionized water and sodium hydroxide

The ether linkages in nonionics are weakly cationic and form oxonium salts with mineral acids. These oxonium salts are more water-soluble than the free nonionic, so that the solubility of the Triton® Nonionic surfactants is greater in acid solutions than in water.

Solubility in nonpolar organic solvents, such as aliphatic hydrocarbons, is generally the reverse of solubility in water. Most of the products are soluble in aromatic hydrocarbons and in polar organic solvents, such as alcohols, ether, etc.

The below table shows the qualitative solubility behavior of these materials.

Solubility of Triton® Octylphenol series at room temperature ⁽¹⁾

| Solvent | Triton® Surfactants | | |
|---|---------------------|-------|-------|
| | X-114 | X-100 | X-405 |
| Water | D | M | M |
| Inorganic Salt Solutions | D | S | S |
| Aqueous Mineral Acids | S ⁽²⁾ | S | S |
| Polar Organic Solvents (alcohols, glycols, ethers, ketones, etc.) | M | M | M |
| Aromatic Hydrocarbons | M | M | I |
| Aliphatic Hydrocarbons | I | I | I |

(1) I = Insoluble; D = Dispersible; M = Miscible in all proportions; S = Soluble

(2) Triton® X-114 is soluble in hydrochloric, phosphoric, and dilute sulfuric acid solutions.

Viscosity of Aqueous Solutions

For the water-soluble members of the series in the 7-13 polyglycol range, the viscosity of the aqueous solutions increases to a maximum on approaching a concentration of 50 percent from either a lower or higher concentration. At room temperature in tap or distilled water, gels may be formed in the concentration range of 40- to 70-percent surfactant; the exact concentration range for gel formation varies with the individual nonionic. Figure 1 shows viscosity vs. concentration ranges in which gels form for the individual products at 25°C and indicate that Triton® X-100 does not form a gel at 50°C in fresh water or at 25°C in 1 molar (approximately 5.8% by weight) sodium chloride (NaCl) solution.

In making up dilute aqueous solutions of the Triton® Nonionics, gel formation can usually be prevented by adding the surfactant to warm water with agitation. If it is necessary to go through the critical gel concentration via the reverse order of addition, the solution should be warmed to decrease the viscosity and the possibility of gelation.

Viscosity at elevated temperature of the higher members is sometimes needed for product transfer. The Table below shows the viscosity of Triton® X-405 (70% solution) at different temperatures.

Viscosity of Triton® X-405 at Various Temperatures

| Temperature, °F | Viscosity ⁽¹⁾ , cP |
|-----------------|-------------------------------|
| | Triton® X-405, 70% solution |
| 40 | 2500 |

| | |
|-----|------|
| 60 | 2000 |
| 80 | 575 |
| 100 | 250 |
| 120 | 125 |

(1) Brookfield LVT, 12 rpm, #2 and #4 spindles.

Compatibility

The alkylphenol polyether alcohol surfactants are compatible with anionic, cationic, and other nonionic products. However, they are discolored when added to dry caustic and anhydrous metasilicate, but they may be used in formulations containing moderate quantities of these alkaline materials without undue discoloration. These surfactants are stable in the presence of mildly alkaline builders, such as sodium carbonate (soda ash), silicates, and phosphates.

Thermal Stability

Thermogravimetric analysis has been used to determine thermal stabilities in air of selected Triton® Nonionic Surfactants sometimes used in high-temperature applications. Weight losses were determined at a programmed heating rate of 10°C/minute, starting at 35°C. (See table below) Additional analytical testing with thermogravimetric analysis (TGA) in conjunction with Fourier Transform Infrared Spectroscope (TGA-FTIR) revealed that under inert (N₂) conditions, observed weight loss is due to product volatilization. Under air atmosphere, oxidative by-products are chiefly responsible for the observed weight losses.

Thermogravimetric Analysis of Triton® Nonionic Surfactants ⁽¹⁾

| | Temperature, °C | | |
|-----------------------------------|--------------------------------|-----|-----|
| | Weight Loss ⁽²⁾ , % | | |
| Triton® Surfactant | 1 | 10 | 50 |
| X-100 | 221 | 291 | 347 |
| X-100 (N ₂ atmosphere) | 210 | 310 | 350 |

(1) Air, unless otherwise indicated.

(2) Percent weight loss is shown after water removal.

Surface Tension

The reduction of surface tension in aqueous solution is a standard test for surface activity. Good wetting agents, detergents, and emulsifiers reduce the surface tension of aqueous solutions appreciably, but this test alone is not adequate for selection of a surface-active agent for a specific application. Surface tension data for some members of this nonionic series in water, acid, and electrolytic solutions are given

in the table below.

Surface Tension ⁽¹⁾ of Triton® Octylphenol Series in Various Solvents ⁽²⁾

| | | Surface Tension, dynes/cm | | | |
|-------------------------------|-----------------------------------|---------------------------|-----|------|-------|
| | | Active Ingredient, wt% | | | |
| Solvent | Triton® Surfactant | 1.0 | 0.1 | 0.01 | 0.001 |
| Water | X-114 | 29 | 29 | 30 | 44 |
| | X-100 | 30 | 30 | 31 | 46 |
| | X-405 (70% Active) ⁽³⁾ | 37 | 37 | 51 | 59 |
| 15% Hydrochloric Acid | X-114 | 30 | 26 | 27 | 30 |
| | X-100 | 30 | 31 | 29 | 44 |
| 20% Calcium Chloride Solution | X-114 | 30 | 28 | 30 | 29 |
| | X-100 | 30 | 30 | 30 | 34 |

(1) All measurements, except as noted, were made with the DuNouy Tensiometer at 25°C.

(2) Surface tension of solvents: distilled water - 72 dynes/cm; 15% hydrochloric acid - 71 dynes/cm; 20% Calcium chloride solution - 79 dynes/cm

(3) Measured with Wilhemy plate at 25°C in deionized water. Concentrations are active and are corrected for the water content in the as-sold material.

Interfacial Tension

The ability to reduce interfacial tension between water and oils is an important property of surface-active agents. Data are shown in the table below for interfacial tension measurements between distilled water and (a) a highly-refined aliphatic mineral oil, "Arcoprime" 90, and (b) an aromatic solvent, toluene, at various concentrations of surfactant. These determinations were made with a DuNouy Tensiometer. Test results depend on whether the surfactant is initially dissolved in the aqueous or oil phase and on the time allowed for establishment of equilibrium of the surfactant between the two phases. In the measurements tabulated, the surfactant was dissolved in the aqueous phase, and a period of five minutes was normally allowed for the attainment of equilibrium. Results also would vary according to the kind of oil and water (tap water, brine, etc.) used.

For the highly aliphatic "Arcoprime" 90, the lowest values are obtained with materials in the chain length region of Triton® X-114 and X-100. Triton® X-114 and X-100 are good stabilizers for toluene emulsions.

Interfacial Tension ⁽¹⁾ of Triton® Octylphenol Series

| | Interfacial Tension, dynes/cm |
|--|-------------------------------|
|--|-------------------------------|

| | "Arcoprime" 90 vs. water | | | | | Toluene vs. water | | | |
|---------------------------|--------------------------|------------|-------------|--------------|--|------------------------|------------|-------------|--------------|
| | Active Ingredient, wt% | | | | | Active Ingredient, wt% | | | |
| Triton® Surfactant | 1.0 | 0.1 | 0.01 | 0.001 | | 1.0 | 0.1 | 0.01 | 0.001 |
| X-114 | 1.5 | 3.0 | 11.5 | 23.5 | | 14.0 | 18.5 | 25.0 | 32.0 |
| X-100 | 1.0 | 2.5 | 10.0 | 21.5 | | 10.5 | 15.5 | 21.5 | 28.5 |
| X-405 | 13.0 | 11.0 | 15.0 | 26.0 | | -- | -- | -- | -- |

(1) All measurements were made with the DuNouy Tensiometer at 25°C

Spreading Coefficients

The spreading coefficient is a measure of the ability of one liquid to spread over another and is calculated by the following equation:

$$S_a = \alpha_b - (\alpha_{ab} + \alpha_a), \text{ where}$$

S_a = spreading coefficient

α_a = surface tension of spreading liquid (water)

α_b = surface tension of liquid on which spreading is done (oil)

α_{ab} = interfacial tension between the two liquids

Data on the spreading coefficients of Triton® Nonionic Surfactants on "Arcoprime" 90 are shown in the table below.

Spreading Coefficients ⁽¹⁾ for Triton® Nonionic Surfactants on Mineral Oil and Toluene

| | Active Concentration of Surfactant, wt% | | | | | | | | |
|---------------------------|---|------------|-------------|--------------|--|-------------|------------|-------------|--------------|
| | vs. Mineral Oil | | | | | vs. Toluene | | | |
| Triton® Surfactant | 1.0 | 0.1 | 0.01 | 0.001 | | 1.0 | 0.1 | 0.01 | 0.001 |
| X-114 | -1.0 | -2.5 | -12.0 | -38.0 | | -15.0 | -19.5 | -27.0 | -48.0 |
| X-100 | -1.5 | -3.0 | -11.5 | -38.0 | | -12.5 | -17.5 | 24.5 | -46.5 |
| Water | -94.5 | -- | -- | -- | | -80.1 | -- | -- | -- |

(1) The more positive the values the more readily the aqueous solution will spread on the solvent.

(2) "Arcoprime" 90

Wetting

An important property of surface-active agents is their ability to improve the rate and degree of the wetting of various surfaces by water, particularly oily or greasy surfaces which are otherwise hard to wet. A commonly used test for wetting power is the Draves Test, which measures the concentration of wetting agent necessary to cause sinking of a weighted cotton skein in a given time in an aqueous solution of the wetting agent. Draves wetting times for most members of this series are given in the Table below. The

lower the concentration of surfactant needed to cause sinking in a given time, the more efficient is the wetting agent.

Draves Wetting Test ⁽¹⁾

| | Active Ingredient, wt%, for Wetting Time of | | |
|--------------------|---|------------|------------|
| Triton® Surfactant | 10 seconds | 25 seconds | 50 seconds |
| X-114 | 0.096 | 0.050 | 0.031 |
| X-100 | 0.092 | 0.048 | 0.028 |
| X-405 (70% active) | 5% gives greater than 300 seconds | | |

(1) AATC 17-1952, 25°C

Foaming

The foaming properties of nonionic surfactants are independent of the pH at which they are used. The amount of foam generated increases with increasing length of the polyether alcohol chain (Table below). The foam that forms is less stable than that obtained with soaps and is not as slippery or as compact.

The values in this table were obtained by the Ross-Miles method, which involves measuring the foam formed by dropping 200 ml of an aqueous solution or dispersion of surfactant a distance of 90 cm into 50 ml of the same liquid in a cylindrical container of 50 cm internal diameter. The test is run at 120°F, and foam heights in millimeters are measured initially and after five minutes.

Ross-Miles Foam Height Tests ⁽¹⁾

| | Foam Height, mm | | | | | | | | | |
|--------------------|------------------------|-------|---------|-------|---------|-------|---------|-------|---------|-------|
| | Active Ingredient, wt% | | | | | | | | | |
| | 1.0 | | 0.3 | | 0.1 | | 0.01 | | | |
| Triton® Surfactant | Initial | 5 min | Initial | 5 min | Initial | 5 min | Initial | 5 min | Initial | 5 min |
| X-114 | 25 | 25 | 20 | 15 | 25 | 22 | 15 | 15 | | |
| X-100 | 228 | 23 | 205 | 40 | 110 | 25 | 20 | 20 | | |
| X-405 | 167 | 15 | -- | -- | 126 | 110 | 32 | 26 | | |

(1) ASTM D 1173-53, 120°F

A study of the foaming properties of members of the OPE series as a function of temperature indicates that below the cloud point of the particular nonionic in aqueous solution, the amount of foam produced is fairly constant with increasing temperature. Above the cloud point, the amount of foam produced drops off sharply to a minimum value. This permits selection of a nonionic that has the desired foaming properties at the temperature at which a specific operation is to be carried out.

Emulsification

Because of their wide range of hydrophilic-lipophilic balance (HLB), the octylphenyl polyether alcohols

offer a broad variety of possible emulsifier combinations. In general, the lowest members of the series are more efficient emulsifiers for aliphatic oils. Aromatic liquids are best emulsified by the hydrophilic materials, such as Triton® X-114 and X-100.

Most Effective Triton® Octylphenol Surfactants for Emulsifying Specific Oils

| Oil | OPE Surfactants Giving Most Stable Emulsions |
|----------|--|
| Kerosene | Triton® X-114 |
| Xylene | Triton® X-114 or X-100 |

For some purposes, a mixture of two or more Triton® Nonionics may provide more effective emulsification than a single material. The nonionic emulsifiers are more versatile than anionic or cationic surfactants because of their lack of reactivity and insensitivity to ions. However, a combination of nonionic and anionic or cationic surfactants may be preferable for some systems.

Solubilization

Many water-insoluble materials can be dispersed or solubilized in water by the octylphenyl polyether alcohols. For example, a blend of three parts of Triton® X-100 with one part of perfume oil may yield a water-soluble perfume. The insoluble products formed by the reaction of soaps with hard water salts or with cationic surfactants can be solubilized or dispersed by adding Triton® X-100 or similar nonionic compounds.

Emulsion Polymerization

Several Triton® Nonionic Surfactants are useful as primary emulsifiers or in mixed anionic-nonionic emulsifying systems in the preparation of acrylic polymer emulsions.

Although octylphenoxyethanol surfactants having HLB values below 16 tend to produce grainy polymer particles ⁽¹⁻³⁾, those having HLB values of 17-18 ⁽¹⁾, such as Triton® X-405, function well as primary emulsifiers. Emulsion polymers formed in the presence of the higher-HLB surfactants have particles of satisfactorily low diameter and exhibit outstanding stability to electrolytes, freeze-thaw cycling, and mechanical stress.

(1) P. Heiberger, *Offic. Dig. Feder. Soc. Paint Technol.*, v. 29, 100 (1957).

(2) W.C. Mast and C.H. Fisher, *Ind. Eng. Chem.*, v. 41, 790 (1949).

(3) "Surface-Active Agents in Polymer Emulsion Coatings," *Rohm and Haas Company Resin Review*, 13(1), 20 (1963).

Two-Stage Redox Copolymerization of Ethyl Acrylate, Methyl Methacrylate, and Acrylic Acid Using Triton X-405 as Emulsifier

| Materials | First Stage | Second Stage |
|-----------------|-------------|--------------|
| Deionized Water | 1000 ml | -- |

| | | |
|--|----------------|----------------|
| Triton® X-405 (70% active) | 30.0 g | 30.0 g |
| Ethyl Acrylate (15 ppm MEHQ) | 260.0 g | 300.0 g |
| Methyl Methacrylate (10 ppm MEHQ) | 155.0 g | 175.0 g |
| Acrylic Acid (250 ppm MEHQ) in deionized water | 4.0 g in 56 ml | 5.0 g in 65 ml |
| Ammonium Persulfate in 1.5 ml of water | 0.6 g | 0.6 g |
| Sodium Hydrosulfite in 6 ml of water | 0.7 g | 0.8 g |

Procedure

Charge water and emulsifier into a 3-L, three-neck, round bottom flask prepared as in the procedure above and cool to 20°C. With stirring and nitrogen purging, add the ethyl acrylate and methyl methacrylate, maintaining the temperature at 28°C. Remove cooling bath (if used) and add the ammonium persulfate and sodium hydrosulfite. Allow exotherm to start and slowly add the acrylic acid solution as the temperature rises to a peak of 60°C. After the peak temperature has been reached, continue stirring and nitrogen purge at 60°C for 60 minutes. Cool the emulsion to 20°C and add the second stage materials in the order listed. After the peak temperature has been reached again, continue stirring and nitrogen purge at 70°C for 60 minutes. Cool the product to 20°C, adjust the pH to 9.5 with 28 percent aqueous ammonia, and strain through cheesecloth. The solids content is about 45.0 percent (calculated 45.5 percent).

Miscellaneous

The intermediate Triton® OPE Nonionics (Triton® X-114, X-100) are widely used as emulsifiers with aromatic solvents, such as xylene and toluene. Triton® X-114 has been used as an additive to increase the extraction of enzymes from plant tissues. ⁽⁴⁾

Because of its high HLB value, Triton® X-405 is an efficient emulsifying agent in emulsion polymerizations. It is also recommended as an emulsifying agent in the preparation of agricultural emulsion concentrates and wettable powders. ⁽⁵⁾

Availability

| Catalog Number | Description | Size |
|----------------|--|--------|
| 807423 | Triton® X-100 | 100 ml |
| 807426 | | 500 ml |
| 194854 | Triton® X-100, Molecular Biology Reagent | 50 ml |
| | | 100 ml |
| | | 250 ml |

| | | |
|--------|---------------|----------------------------|
| 193971 | Triton® X-114 | 100 ml 250 ml 500 ml |
| 152411 | Triton® X-405 | 100 ml 500 ml |

References:

1. R.L. Reed and J.J. Taber (to Gulf Research & Development Co.), U.S. **3**, 147,806 (Sept. 8, 1964).
2. J.W. Graham, W.M. McCardell, J.O. Osoba, and J.G. Richardson (to Esso Research and Engineering Co.), U.S. **2**, 792,894 (May 21, 1957).
3. T. Lewandowski (to Bonewitz Chemicals, Inc.), U.S. **3**, 218,260 (Nov. 16, 1965).
4. A.M. Badran and D.E. Jones, *Nature*, **v.206**:4984, 622-4 (1965).
5. G.C. Riley and E.A. Nolan, *Rohm and Haas Co.*, U.S. **3**, 102,070 (Aug. 27, 1963).
6. Womack, M.D., et al., *Biochim. Biophys. Acta*, **v. 733**, 210 (1983)
7. Matson, R.S. and Goheen, S.C., *LC-GC*, **v. 4(7)**, 624 (1986)