SULFONIC ACIDS

Sulfonic (or sulphonic) acids are classically defined as a group of organic acids which contain one or more sulfonic, $-SO_3H$, groups. The focus of this chapter is an overview of organic sulfonic acids which have the formula RSO_3H, where the R-group may be derived from many different sources. Typical R-groups are alkane, alkene, alkyne, and arene. The R-group may contain a wide variety of secondary functionalities such as amine, amide, carboxylic acid, ester, ether, ketone, nitrile, phenol, etc. Sulfonic acid derivatives are used industrially on a large scale in the manufacture of surfactants, dyes, inks, dispersing agents, and polymers. Sulfonic acids also find broad application as catalysts in both alkylation (qv) processes and general organic reactions. Sulfonic acid derivatives have found more esoteric applications in the areas of custom organic syntheses and biological research. Sulfonic acids derivatives, where the R-group is derived from an inorganic source such as a halide, oxygen (ie, sulfate), or amine (ie, sulfamic acid), are not discussed herein to a great extent. These last are often referred to as sulfuric acid derivatives (see Chlorosulfuric acid).

1. Physical Properties

The physical properties of sulfonic acids vary greatly depending on the nature of the R-group. Sulfonic acids are found in both the solid and liquid forms at room temperature. No examples of gaseous sulfonic acids are known as of the mid-1990s. Sulfonic acids can be described as having similar acidity characteristics to sulfuric acid. Sulfonic acids are prone to thermal decomposition, ie, desulfonation, at elevated temperatures. However, several of the alkane-derived sulfonic acids show excellent thermal stability, as shown in Table 1. Arene-based sulfonic acids are thermally unstable. These must be distilled under extreme vacuum conditions using a minimal amount of heating to avoid thermal decomposition. Polyaromatic compounds, such as 1-naphthalenesulfonic acid and 2-naphthalenesulfonic acids [83-47-2] and [120-18-3], respectively, readily decompose upon attempted distillation even at very high vacuum.

Sulfonic acids are such strong acids that in general they can be considered greater than 99% ionized. The pK_a value for sulfuric acid is -2.8 as compared to the pK_a values of -1.92, -1.68, and -2.8 for methanesulfonic acid, ethanesulfonic acid, and benzene sulfonic acid, respectively (3). Trifluoromethanesulfonic acid [1493-13-6] has a pK_a of less than -2.8, making it one of the strongest acids known (4, 5). Trifluoromethanesulfonic acid is also one of the most robust sulfonic acids. Heating this material to 350°C causes no thermal breakdown (6).

The x-ray crystal structures of the many sulfonic acid derivatives, such as methanesulfonic acid, have been determined (7). A large amount of theoretical work has been compiled for simple sulfonic acid radical, anion, and cation species, including energies, dipole moments, optimized bond lengths and angles, Mulliken atomic charges, d-orbital occupancies, ionization potential, proton affinities, and homolytic hydrogen atom bond dissociation energies (8). Experimental data have also been compiled for sulfonic acids on physical properties such as heats of formation and heats of combustion (9).

Table 1. Physical Properties of Sulfonic Acids[a]

Acid	CAS Registry Number	Mp, °C	Bp,[b] °C	Density d_4^{25}, g/cm^3
methanesulfonic acid	[75-75-2]	20	122	1.48
ethanesulfonic acid	[594-45-6]	−17	123	1.33
propanesulfonic acid	[28553-80-2]	−37	159	1.19
butanesulfonic acid	[30734-86-2]	−15	149	1.19
pentanesulfonic acid	[35452-30-3]	−16	163	1.12
hexanesulfonic acid	[13595-73-8]	16	174	1.10
benzenesulfonic acid	[98-11-3]	44	172[c]	
p-toluenesulfonic acid	[104-15-4]	106	182[c]	
1-naphthalenesulfonic acid	[85-47-2]	78	dec	
2-naphthalenesulfonic acid	[120-18-3]	91	dec	1.44
trifluoromethanesulfonic acid	[1493-13-6]	none	162[d]	1.70

[a]Refs. 1 and 2.
[b]At 133 Pa (1 mm Hg) unless otherwise noted.
[c]At 13.3 Pa (0.1 mm Hg).
[d]At 101.3 kPa = 760 mm Hg.

2. Chemical Properties

Sulfonic acids are prepared on a commercial scale by the sulfonation of organic substrates using a variety of sulfonating agents, including sulfur trioxide [7446-11-9] (diluted in air), sulfur trioxide (in sulfur dioxide [7446-09-5]), sulfuric acid [7664-93-9], oleum [8014-95-7] (fuming sulfuric acid), chlorosulfuric acid [7790-94-5], sulfamic acid [5329-14-6], trialkylamine–sulfur trioxide complexes, and sulfite ions. Other methods of sulfonic acid production, which are practiced on an industrial scale, include the oxidation of thiols (qv), sulfide, disulfides, sulfoxides (qv), sulfones, and sulfinic acids (see Sulfonation and sulfation). A preparative review of sulfonic acids has been compiled and the variety of functionalities that may be present in a sulfonic acid derivative is wide. Sulfonic acids having amide, arene, alkane, alkene, alkyne, ester, hydroxyl, and nitrile functionality are known (10) (see Sulfur compounds). This diversity leads to very rich reaction chemistry involving sulfonic acids and their corresponding sulfonates.

2.1. General Reaction Chemistry of Sulfonic Acids

Sulfonic acids may be used to produce sulfonic acid esters, which are derived from epoxides, olefins, alkynes, allenes, and ketenes, as shown in Figure 1 (10). Sulfonic acids may be converted to sulfonamides via reaction with an amine in the presence of phosphorus oxychloride [10025-87-3], POCl$_3$ (11). Because sulfonic acids are generally not converted directly to sulfonamides, the reaction most likely involves a sulfonyl chloride intermediate. Phosphorus pentachloride [10026-13-8] and phosphorus pentabromide [7789-69-7] can be used to convert sulfonic acids to the corresponding sulfonyl halides (12, 13). The conversion may also be accomplished by continuous electrolysis of thiols or disulfides in the presence of aqueous HCl [7647-01-0] (14) or by direct sulfonation with chlorosulfuric acid. Sulfonyl fluorides are typically prepared by direct sulfonation with fluorosulfuric acid [7789-21-1], or by reaction of the sulfonic acid or sulfonate with fluorosulfuric acid. Halogenation of sulfonic acids, which avoids production of a sulfonyl halide, can be achieved under oxidative halogenation conditions (15).
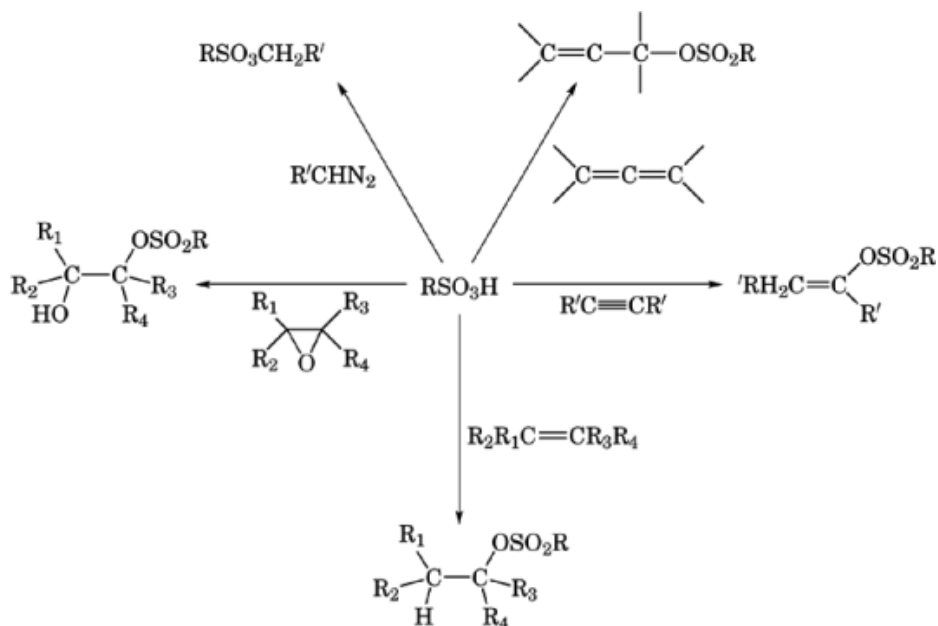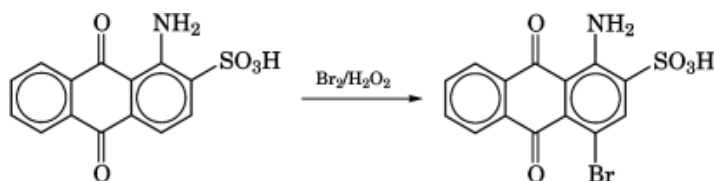
**Fig. 1.**   Reaction chemistry of sulfonic acids.

Sulfonic acids are prone to reduction with iodine [7553-56-2] in the presence of triphenylphosphine [603-35-0] to produce the corresponding iodides. This type of reduction is also facile with alkyl sulfonates (16). Aromatic sulfonic acids may also be reduced electrochemically to give the parent arene. However, sulfonic acids, when reduced with iodine and phosphorus [7723-14-0], produce thiols (qv). Amination of sulfonates has also been reported, in which the carbon–sulfur bond is cleaved (17). Ortho-lithiation of sulfonic acid lithium salts has proven to be a useful technique for organic syntheses, but has little commercial importance. Optically active sulfonates have been used in asymmetric syntheses to selectively *O*-alkylate alcohols and phenols, typically on a laboratory scale. Aromatic sulfonates are cleaved, ie, desulfonated, by uv radiation to give the parent aromatic compound and a coupling product of the aromatic compound, as shown, where Ar represents an aryl group (18).

$$\text{ArSO}_3\text{H} \xrightarrow[(-\text{SO}_3^-)]{hv} \text{ArH} + \text{Ar}\!-\!\!\text{Ar}$$
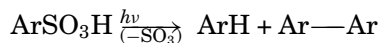
Sulfonic acids may be subjected to a variety of transformation conditions, as shown in Figure 2. Sulfonic acids can be used to produce sulfonic anhydrides by treatment with a dehydrating agent, such as thionyl chloride [7719-09-7]. This transformation is also accomplished using phosphorus pentoxide [1314-56-3]. Sulfonic anhydrides, particularly aromatic sulfonic anhydrides, are often produced *in situ* during sulfonation with
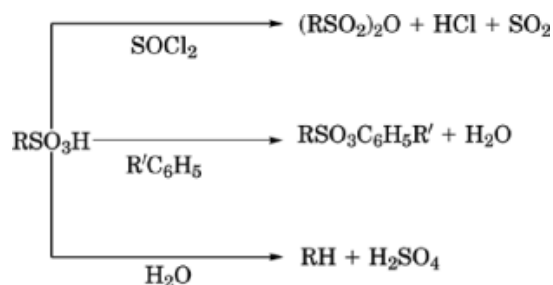
Fig. 2. Sulfonic acid transformations.
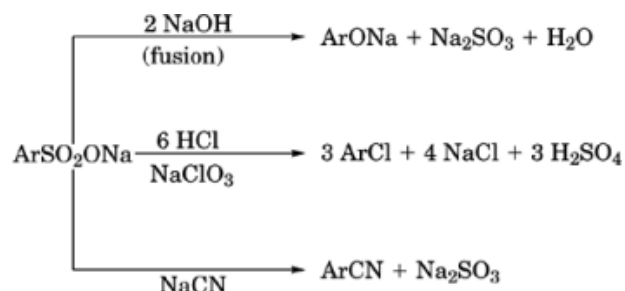
**Fig. 3.** Cleavage reactions of sulfonates where Ar is an aryl group.

sulfur trioxide. Under dehydrating conditions, sulfonic acids react with substituted aromatic compounds to give sulfone derivatives.

Sulfonic acids may be hydrolytically cleaved, using high temperatures and pressures, to drive the reaction to completion. As would be expected, each sulfonic acid has its own unique hydrolytic desulfonation temperature. Lower alkane sulfonic acids possess excellent hydrolytic stability, as compared to aromatic sulfonic acids which are readily hydrolyzed. Hydrolytic desulfonation finds use in the separation of isomers of xylene sulfonic acids and other substituted mono-, di-, and polysulfonic acids.

The cleavage products of several sulfonates are utilized on an industrial scale (Fig. 3). The fusion of aromatic sulfonates with sodium hydroxide [1310-73-2] and other caustic alkalies produces phenolic salts (see Alkylphenols; Phenol). Chlorinated aromatics are produced by treatment of an aromatic sulfonate with hydrochloric acid and sodium chlorate [7775-09-9]. Nitriles (qv) (see SUPPLEMENT) can be produced by reaction of a sulfonate with a cyanide salt. Arenesulfonates can be converted to amines with the use of ammonia. This transformation is also rather facile using mono- and dialkylamines.

2.2. Miscellaneous Reactions

Aromatic sulfonic acid derivatives can be nitrated using nitric acid [52583-42-3], HNO_3, in H_2SO_4 (19). Sultones may be treated with hydrazine derivatives to give the corresponding ring-opened sulfonic acid (20).
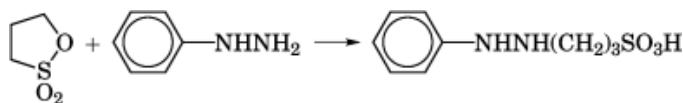
Catalytic reduction of secondary functionalities in sulfonates, in which the sulfonate moiety is unchanged, is accomplished using standard hydrogenation techniques (21). Sulfonic acids may be converted to the corresponding silyl esters in very high yields (22).
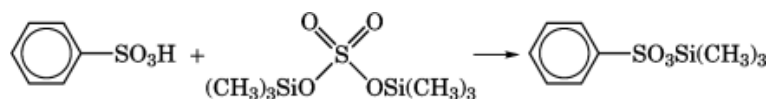
3. Production

At the end of 1994, there were four primary methods of sulfonic acid production in the United States. The methods were falling film sulfonation (791,518 metric tons), representing 71% of production and using gaseous SO_3; oleum sulfonation (219,085 t), representing 19% of production; chlorosulfuric acid sulfonation (88,452 t), representing 8% of production; and SO_3 solvent-based sulfonation (26,308 t), representing 2% of production in SO_2 (22, 23). These 1994 U.S. acid production numbers do not include minor sulfonic acid production via the use of low throughput continuous, batch SO_3 (100 wt %), H_2SO_4 (20–30 wt %), oleum (30 wt %), and sulfamic acid.

The vast majority of sulfonic acids were produced in the United States using continuous falling film sulfonation technology which utilizes vaporized SO_3 mixed with air. This technology dominates the sulfonation industry owing to the capability of high product throughput and low by-product waste streams. Of the other three methods of sulfonic acid production, the use of sulfur trioxide, where sulfur dioxide is the solvent, is perhaps the most tedious, owing to handling, recovery, and safety issues inherent in the use of the solvent.

4. Economic Aspects

In 1991, over 1×10^6 t sulfonic acids were produced in the United States (24). The materials, for the most part, were used as intermediates for the manufacture of sulfonates in the detergent market, dye manufacture, dispersing agents, catalysts, polymers, etc. Production of dodecylbenzenesulfonic acids derivatives dominated the sulfonic acid market (Table 2). These had a 38% overall share. The differences between the production tons and the tons sold is accounted for by in-plant use by various manufacturers verses merchant market production.

As of the end of 1991, there were over 60 manufacturers of sulfonic acids and sulfonates in the United States (25). In 1995, Stepan Company was the largest merchant manufacturer of sulfonic acids in the United States, having a total sulfonation–sulfation capacity of over 522,000 t (26). In 1993, the largest volume sulfonic acid produced in the United States was linear alkylbenzenesulfonic acid, which translated to 346,000 t of linear alkylbenzenesulfonates, accounting for 25% of U.S. consumption of surfactants (qv) (23). Table (3) shows a summary of the major sulfonic acid and sulfonate producers in the United States as of the end of 1991. Of these, the largest nonmerchant market producers of sulfonic acids were The Procter & Gamble Company, Colgate-Palmolive Company, and Lever Brothers Company. Elf Atochem North America is the sole U.S. producer of methanesulfonic acid.

Table 2. U.S. Production, Sales, and Value of Sulfonic Acids[a]

					Production	
Sulfonic acid[b]	Production, t	% of Total	Sales, t	Av. price, $/t	t	% of Total
dodecylbenzenesulfonic acid	157, 205	15.7	105,201	790	83,361,000	124,191,950
Ca salt	2, 431	0.2	1,743	3, 140	5,476,000	7,633,340
IPA salt	4, 258	0.4	3,937	1, 540	6,073,000	6,557,320
K salt	18					
Na salts	216, 334	21.6	24,997	1, 630	40,638,000	352,624,420
TEA salt	1, 548	0.2	1,531	1, 770	2,715,000	2,739,960
liginsulfonic acid						
Ca salt	292, 780	29.3	283,561	110	31,607,000	32,205,800
Na salt	87, 816	8.8	87,140	340	29,982,000	29,857,440
tridecylbenzenesulfonic acid, Na salt	11, 738	1.2	709	1, 650	1,167,000	19,367,700
xylenesulfonic acid, Na salt	34, 076	3.4	29,973	730	21,888,000	24,875,480
all other sulfonic acids and salts	192, 451	19.2	116,438	1, 020	118,775,000	196,300,020
Totals	1, 000, 655	100.0	655,230		341,682,000	796,353,430

[a]Ref. 24.

[b]IPA = isopropylamine; TEA = triethanolamine.

5. Quality and Storage

The quality of sulfonic acids produced as intermediates on an industrial scale is important to detergent manufacturers. Parameters such as color, water, free oil (unsulfonated material), and acid value (actual sulfonic acid) are all factors that determine the quality of a sulfonic acid. The quality of the feedstock prior to sulfonation, such as iodine value, water content, and sulfonatability, affects the quality of the sulfonic acid produced. Sulfonation conditions, such as temperature, molar ratio, rate, etc, also affect the quality of sulfonic acid.

Anhydrous sulfonic acids, particularly linear alkylbenzenesulfonic acids, are typically stored in stainless steel containers, preferably type 304 or 316 stainless steel. Use of other metals, such as mild steel, contaminates the acid with iron (qv), causing a darkening of the acid over time (27). The materials are usually viscous oils which may be stored and handled at 30–35°C for up to two months (27). All other detergent-grade sulfonic acids, eg, alcohol sulfates, alcohol ether sulfates, alpha-olefin sulfonates, and alpha-sulfomethyl esters, are not stored owing to instability. These are neutralized to the desired salt.

6. Analytical and Test Methods

Modern analytical techniques have been developed for complete characterization and evaluation of a wide variety of sulfonic acids and sulfonates. The analytical methods for free sulfonic acids and sulfonate salts have been compiled (28). Titration is the most straightforward method of evaluating sulfonic acids produced on either a laboratory or an industrial scale (29, 30). Spectroscopic methods for sulfonic acid analysis include ultraviolet spectroscopy, infrared spectroscopy, and ^{1}H and ^{13}C nmr spectroscopy (31). Chromatographic separation techniques, such as gc and gc/ms, are not used for free sulfonic acids owing to characteristics such as acidity and lack of volatility. Typically the sulfonic acid must be neutralized, derivatized, and/or desulfonated (pyrolysis or chemical) prior to evaluation (32). Mixtures of sulfonic acids are typically separated on the laboratory scale using standard chromatographic methods, such as column chromatography, paper chromatography, tlc, and hplc (33). Separation of sulfonic acid mixtures on the industrial scale is not common. Neutralized sulfonic acid mixtures have been analyzed using infrared and ^{1}H and ^{13}C nmr (30). Modern separation techniques of sulfonates include liquid chromatography and ion chromatography (34–36) (see Chromatography).

Table 3. U.S. Sulfonic Acid Producers as of 1991[a,b]

Sulfonic acid type	American Cyanamid Co.	Burlington Industries	CNC International Inc.	Colgate-Palmolive Co.	Chemithon Corp.	Dial Corp.	Dow Chemical Co.	Eastern Color & Chemical Co.	E. I. du Pont de Nemours & Co.	Exxon Chemical Americas	Finetex, Inc.	Georgia-Pacific Corp.	Grant Industries	Grifftex Chemical
alkylbenzenesulfonic acids and salts	+	+	+	+	+	+	+	+	+	+			+	
benzenesulfonic acid														
cumene sulfonic acid and salts														
toluene sulfonic acid and salts														
xylenesulfonic acid and salts								+						
ligninsulfonates												+		
naphthalenesulfonic acid and salts								+	+			+	+	
sulfosuccinamic acid and derivatives	+							+	+					+
taurine-based sulfonic acids and salts		+	+						+	+				
other sulfonic acids with amide linkage											+			
sulfosuccinic acid esters	+	+	+				+	+	+	+	+			+
other sulfonic acids with ester linkage											+			
sulfonic acids with ether linkage														
mixed alkane sulfonic acids and salts														
mixed linear olefin sulfonates														
water-soluble petroleumsulfonic acids														
all other sulfonic acids														

[a] Ref. 24.
[b] A list of other, smaller sulfonic manufacturers is also available (24).

Table 3. (Continued)

Sulfonic acid type	Harcros Chemicals, Inc.	Henkel Corp.	Hoechst Celanese Corp.	ICI Americas, Inc.	J. L. Prescott Co.	Lever Brothers Co.	Lignotech (U.S.), Inc.	Lonza, Inc.	Mona Industries	National Starch & Chem.	Pilot Chem. Co.	Procter & Gamble Co.	Rhône-Poulenc, Inc.	Ruetgers-Nease Chemical Co.
alkylbenzenesulfonic acids and salts	+	+	+	+	+	+		+			+	+	+	+
benzenesulfonic acid														
cumene sulfonic acid and salts		+												+
toluene sulfonic acid and salts		+										+		+
xylenesulfonic acid and salts		+		+							+			+
ligninsulfonates							+							
naphthalenesulfonic acid and salts		+		+										
sulfosuccinamic acid and derivatives		+							+					
taurine-based sulfonic acids and salts			+										+	
other sulfonic acids with amide linkage			+											
sulfosuccinic acid esters		+	+						+	+			+	
other sulfonic acids with ester linkage						+					+		+	
sulfonic acids with ether linkage												+		
mixed alkane sulfonic acids and salts														
mixed linear olefin sulfonates													+	
water-soluble petroleumsulfonic acids											+			
all other sulfonic acids														

Table 3. (Continued)

Sulfonic acid type	Sandoz Chemical Corp.	Stepan Co.	Vista Chemical, Inc.	Witco Corp.	Westvaco Corp.
alkylbenzenesulfonic acids and salts		+	+	+	
benzenesulfonic acid				+	
cumene sulfonic acid and salts		+			
toluene sulfonic acid and salts			+	+	
xylenesulfonic acid and salts	+	+		+	
ligninsulfonates					+
naphthalenesulfonic acid and salts					
sulfosuccinamic acid and derivatives				+	
taurine-based sulfonic acids and salts					+
other sulfonic acids with amide linkage					
sulfosuccinic acid esters				+	
other sulfonic acids with ester linkage		+			
sulfonic acids with ether linkage					
mixed alkane sulfonic acids and salts		+		+	
mixed linear olefin sulfonates		+			+
water-soluble petroleumsulfonic acids				+	
all other sulfonic acids		+			

Table 4. Toxicity Profiles for Sulfonic Acids[a]

Compound	CAS Registry Number	Toxicity profile
benzenesulfonic acid	[98-11-3]	highly irritating to skin, eyes, and mucous membranes; oral LD_{50} (rat) = 890 mg/kg vs 3800 mg/kg for benzene
dodecylbenzene sulfonic acid	[27176-87-0]	moderately toxic by ingestion; oral LD_{50}(rat) = 650 mg/kg vs 34,000 mg/kg for dodecylbenzene
dodecylbenzene sulfonic acid (sodium salt)	[25155-30-0]	skin and eye irritant; oral LD_{50} (rat) = 1,260 mg/kg
m-nitrobenzenesulfonic acid (sodium salt)	[98-47-5]	oral LD_{50} (rat) = 11,000 mg/kg vs 640 mg/kg for nitrobenzene
m-aminobenzenesulfonic acid	[121-47-1]	oral LD_{50} (rat) = 12,000 mg/kg vs 440 mg/kg for aminobenzene
methanesulfonic acid	[75-75-2]	strong irritant to eyes, lungs, and mucuous membranes
chlorosulfuric acid (chlorosulfonic acid)	[7790-94-5]	highly irritating and corrosive to eyes, skin, mucous membranes; poison; acute toxic effects
fluorosulfuric acid (fluorosulfonic acid)	[7789-21-1]	highly irritating to skin, mucous membranes; aquatic toxicity rating TL = 100 − 110 ppm after 96 h
trifluoromethanesulfonic acid	[1493-13-6]	oral LD_{50} (mouse) = 112 mg/kg
p-toluenesulfonic acid	[104-15-4]	highly irritating to skin, mucous membranes; oral LD_{50} (rat) = 2,480mg/kg vs 5,000 mg/kg for toluene
1-naphthalenesulfonic acid	[85-47-2]	oral LD_{50} (rat) = 420 mg/kg vs 1,780 mg/kg for naphthalene
2-naphthalenesulfonic acid	[120-18-3]	oral LD_{50} (rat) = 400 mg/kg vs 1,780 mg/kg for naphthalene
3,5-dimethylbenzenesulfonic acid (m-xylene-m-sulfonic acid)	[18023-22-8]	ip LD_{50} (mouse) = 500 mg/kg

[a]Refs. (37–39).

7. Health and Safety Factors

In general, unneutralized sulfonic acids are regarded as moderate to highly toxic substances, as shown in Table 4. However, slight detoxification, via the introduction of a sulfonic acid moiety, is observed for nitrobenzene and aminobenzene. This effect has been explained by the fact that sulfonated materials are more hydrophilic than the parent compounds and thus are more readily excreted from the body in the urine (40). Sulfonic acids emit toxic SO_x fumes upon heating to decomposition (38). Halogenated sulfonic acids, such as trifluoromethane sulfonic acid, also release toxic halogen-containing fumes when heated to decomposition (38). Sulfonic acid esters, especially those derived from low molecular weight alcohols, should not be heated above 120°C, as these materials have been reported to explosively decompose (41). Sulfonic acids have essentially the same corrosive characteristics as does concentrated sulfuric acid. Detergent-based sulfonic acids pose a contact hazard, as they are very corrosive to the skin.

When sulfonic acids are neutralized to sulfonic acid salts, the materials become relatively innocuous and low in toxicity, as compared to the parent sulfonic acid (see Table 4). The neutralized materials cause considerably less eye and skin irritation. The most toxic route of entry for sulfonic acid salts is ingestion (39). The toxicity of neutralized sulfonic acids, especially detergent sulfonates, has been directly related to the foaming capability of the material. In general, the higher the foaming power, the lower the toxicity (39). Sulfonates that are absorbed into a living system are readily distributed and excreted. A strong binding of sulfonates, such as the sodium salts of methanesulfonic and benzenesulfonic acids, to proteins has been observed (39). The mechanism of linear alkylbenzene sulfonate degradation has been shown to produce alkylbenzene and sulfate products (42). The alkyl chains are further degraded by standard C-2-β-oxidation. Mutagenic behavior has been observed for materials such as alkyl-substituted butanethiolsulfonates, owing to a strong alkylation capability (43, 44). The mutagenicity of sulfonic acid-based azo dyes has also been extensively studied (45).

8. Environmental Issues

Linear alkylbenzenesulfonic acid is the largest intermediate used for surfactant production in the world. In the United States it has been determined that 2.6 g/d of material is used per inhabitant (46). Owing to the large volumes of production and consumption of linear alkylbenzenesulfonate, much attention has been paid to its biodegradation and a series of evaluations have been performed to thoroughly study its behavior in the environment (47–56). Much less attention has been paid to the environmental impact of other sulfonic acid-based materials.

Linear alkylbenzenesulfonate showed no deleterious effect on agricultural crops exposed to this material (54, 55). Kinetics of biodegradation have been studied in both wastewater treatment systems and natural degradation systems (48, 57, 58). Studies have concluded that linear alkylbenzenesulfonate does not pose a risk to the environment (50). Linear alkylbenzenesulfonate has a half-life of approximately one day in sewage sludge and natural water sources and a half-life of one to three weeks in soils. Aquatic environmental safety assessment has also shown that the material does not pose a hazard to the aquatic environment (56).

Qualitative and quantitative methods for aromatic sulfonic acid determination in wastewater have been developed (59, 60). Standard test methods have also been established for biodegradability of alkylbenzenesulfonates (61). These methods, which involve two tests, have been established to determine if linear alkylbenzenesulfonate is sufficiently removed via standard sewage treatment. The tests are a presumptive test, involving yeast cultures, and a confirming test, involving activated sludge. As a rule of thumb, if the presumptive test method produces a $\geq 90\%$ reduction in linear alkylbenzenesulfonate, the material may be considered sufficiently biodegradable, and no further treatment is needed prior to release into the environment. A $<80\%$ reduction in linear alkylbenzenesulfonate requires further testing to determine if a material has a unsatisfactory biodegradation profile. More recently, studies involving the monitoring of linear alkylbenzenesulfonate degradation in lagoon-type wastewater treatment facilities have shown $>97\%$ consumption, well above the required level of 90% consumption (62).

Branched alkylbenzenesulfonic acids and the corresponding sulfonates have been essentially eliminated from use in the commercial laundry detergent market. The biodegradation profile of branched alkylbenzenesulfonates was found to be unacceptable owing to several problems, the most important of which was slow and incomplete breakdown (49). Residual components caused foaming in sewage treatment plants and in natural waterways. Undegraded material was finding its way into freshwater sources and negatively effecting aquatic animal and vegetable life.

## 9. Uses

9.1. Surfactants and Detergents Uses

Perhaps the largest use of sulfonic acids is the manufacture of surfactants (qv) and surfactant formulations. This is primarily owing to the dominance of linear alkylbenzenesulfonic acid production for detergent manufacture. In almost all cases, the parent sulfonic acid is an intermediate which is converted to a sulfonate prior to use. The largest volume uses for sulfonic acid intermediates are the manufacture of heavy-duty liquid and powder detergents, light-duty liquid detergents, hand soaps (see Soap), and shampoos (see Hair preparations). The anionic components of these materials are based primarily on linear alkylbenzenesulfonates, alkenyl sulfonates, and sulfo fatty alkyl esters (63).

Specialty sulfonic acid-based surfactants make up a rather large portion of surfactant production in the United States. Approximately 136,000 metric tons of specialty sulfonic acid-based surfactants were produced in 1992, which included alpha-olefin sulfonates, sulfobetaines, sulfosuccinates, and alkyl diphenyl ether

disulfonates (64). These materials found use in the areas of household cleaning products, cosmetics (qv), toiletries, emulsion polymerization, and agricultural chemical manufacture.

Lignosulfates, a complex mixture containing sulfonated lignin, are used as dispersing agents, wetting agents, binding agents, and sequestering agents (see Lignin) (65). Dry forms of the materials are used as road binders, concrete additives, animal feed additives, and in vanillin (qv) production (66). Lignin sulfonates are typically produced by the sulfonation/neutralization of lignin or as a by-product of sulfite wood pulping (see Pulp).

Naphthalenic, lignin, and melamine-based sulfonic acids are used as dispersion and wetting agents in industry. The condensation product (1) of formaldehyde [50-00-0] and 2-naphthalene sulfonic acid sodium salt [532-02-5] has been widely used as a cement dispersant for increasing flowability and strength (67). The sulfonate (1) is also widely used as a dispersing agent in dyestuff manufacture and high temperature dyeing of polyester fibers with disperse dyes and vat dyeing of cotton fibers (68). In 1989, (1) was the major synthetic organic leather tanning agent produced in the United States (69). A derivative of (1) based on 4-aminobenzenesulfonic acid has also been produced on the commercial scale (70).

(1)
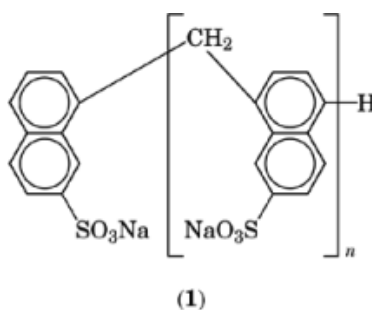
Other commercial naphthalene-based sulfonic acids, such as dinonylnaphthalene sulfonic acid, are used as phase-transfer catalysts and acid reaction catalysts in organic solvents (71). Dinonylnaphthalene sulfonic acid is an example of a water-insoluble synthetic sulfonic acid.

Benzenedisulfonic acid [831-59-4] (disodium salt), produced by the neutralization of the disulfonic acid with sodium sulfite [7757-83-7], is used in the manufacture of resorcinol [108-46-3] (1,3-benzenediol) (2), a chemical component found in rubber products and wood adhesives (72). The disodium salt is fused with sodium hydroxide, dissolved in water, and acidified to produce resorcinol, which is isolated via extraction (73).


(2)
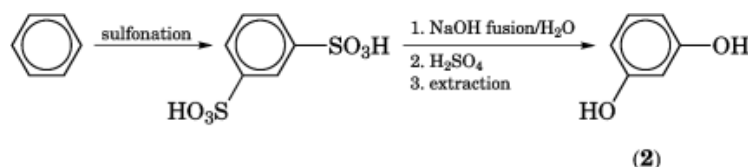
9.2. Sulfonic Acid-Based Dyestuffs

Sulfonic acid-derived dyes are utilized industrially in the areas of textiles (qv), paper, cosmetics (qv), foods, detergents, soaps, leather, and inks, both as reactive and disperse dyes. Of the principal classes of dyes, sulfonic acid derivatives find utility in the areas of acid, azoic, direct, disperse, and fiber-reactive dyes. In 1994, 120,930 t of synthetic dyes were manufactured in the United States, of which 5,600 t were acidic (74). The three largest manufacturers of sulfonic acid-based dyes for use in the United States are BASF, Bayer, and Ciba-Geigy.
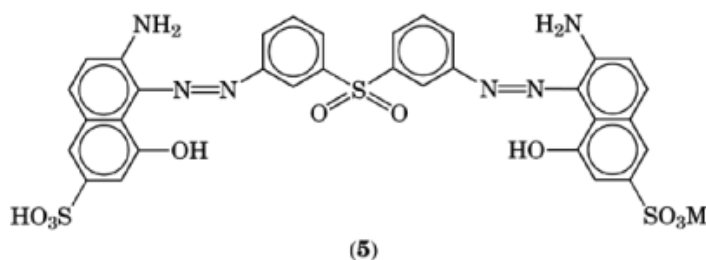
13 SULFONIC ACIDS

Sulfonic acid-based azo dyes (qv) and intermediates are characterized by the presence of one or more azo, R–N=N–R, groups. An example of a water-soluble polysulfonic acid-based azo dye (**3**), where M is a metal, typically Na, for use in ink-jet printers, is shown (75).

(**3**)
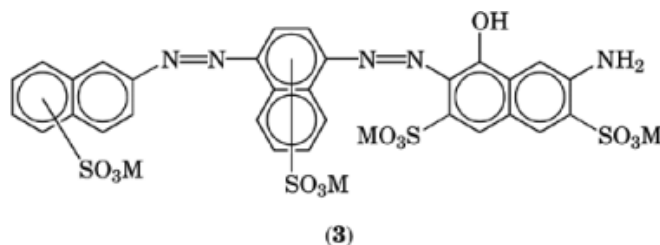
The material, made by a two-step diazotization of each naphthalenic sulfonic acid derivative, is typically used in the form of the neutralized sodium salt. A similar sulfonic acid-based azo dye (**4**) which falls into the class of reactive dyes is also shown (76). This compound, made similarly to (**3**), is used as a blue dyestuff for cotton and wool.

(**4**)
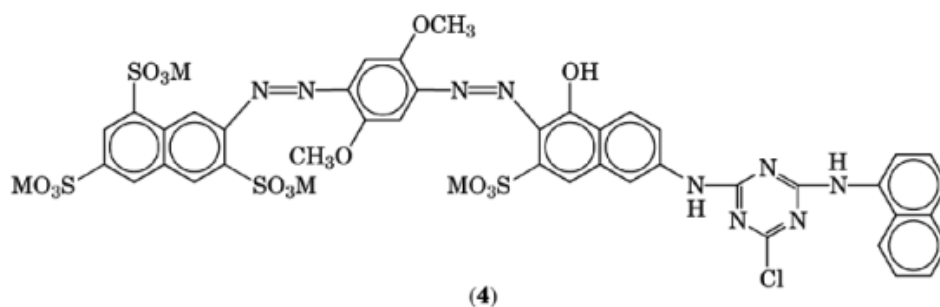
Changes in the backbone of the sulfonic acid azo dyes often produce drastic changes in properties of the materials. The disulfonic acid (**5**) is somewhat similar to (**3**), but is used to color leather red (77). More esoteric dyes have also been developed based on sulfonic acid metal complexes and chitosan-derived materials (78, 79).

(**5**)

9.3. Amide-Based Sulfonic Acids

The most important amide-based sulfonic acids are the alkenylamidoalkanesulfonic acids. These materials have been extensively described in the literature. A variety of examples are given in Table 5. Acrylamidoalkanesulfonic acids are typically prepared using technology originally disclosed by Lubrizol Corporation in 1970 (80). The chemistry involves an initial reaction of an olefin, which contains at least one allylic proton, with

an acyl hydrogen sulfate source, to produce a sulfonated intermediate. This intermediate subsequently reacts with water, acrylonitrile, and sulfuric acid.

Lubrizol Corporation manufactures and markets one of the most commercially successful acrylamidoalkanesulfonic acids, 2-acrylamido-2-methylpropanesulfonic acid, under the trademark of AMPS monomer (81). The material, a highly reactive, water-soluble sulfonic acid, is also soluble in many polar organic solvents. It shows excellent hydrolytic stability properties, along with thermal stability. AMPS monomer contributes lubricity and resistance to divalent cation precipitation in high performance polymer applications. Acrylamidoalkanesulfonic acids are used in a wide variety of applications. AMPS monomer in particular is used in surfactant applications, brass electroplating, printing inks, clear antifog coatings, permanent press and soil-release agents, textile sizes, and dye receptivity agents. Acrylamidoalkanesulfonic acids have also found application as leather finishing agents (82), hydraulic cement admixtures (83), curing accelerators for aminoplast resins (84), acrylic thermosetting coatings (85), and enhanced petroleum recovery (86).

Other amide-based sulfonic acid derivatives find a wide variety of commercial uses. Sulfonic acid amide derivatives, such as N-(2-chlorophenyl)-1-chloromethane sulfonamide [30064-44-9], are utilized in insecticide compositions (87). Acrylimidoaminoethanesulfonic acids and their derivatives are used as flocculating agents (qv) and are also used in the preparation of polymers. These materials are prepared by the sequential reaction of acrylonitrile [107-13-1] with SO_3, 2,2-dimethylpropane, and NH_3 [7664-41-7] at low temperatures (-30 to $-75°C$) (88). Amidoalkanesulfonic acids are used as dispersing agents for calcium soaps. They are typically prepared by the reaction of nitriles with olefins and concentrated sulfuric acid or oleum (89). Derivatives of these materials have also been prepared by treatment of nitriles with 2-hydroxyalkanesulfonic acids in concentrated sulfuric acid, in the presence of various vinyl compounds, to give polymeric dispersing agents (90).

9.4. Fluorinated and Chlorfluorinated Sulfonic Acids

The synthesis of chlorinated and fluorinated sulfonic acids has been extensively reviewed (91, 92). The literature discusses the reaction of dialkyl sulfides and disulfides, sulfoxides and sulfones, alkanesulfonyl halides, alkanesulfonic acids and alkanethiols with oxygen, hydrogen chloride, hydrogen fluoride, and oxygen–chloride–hydrogen fluoride mixtures over metal halide catalysts, such as $CuCl_2$–KCl and $MnBr_2$–$LaCl_3$, to give the respective acids. The reaction of Cl_2CHSH with oxygen–hydrogen fluoride over $CuCl_2$–KCl gives CF_3SO_3H, $ClCF_2SO_3H$ [73043-98-8], Cl_2CFSO_3H [77801-23-1], CHF_2SO_3H [40856-11-9], and $ClCHFSO_3H$ [40856-08-4] (see Fluorine compounds).
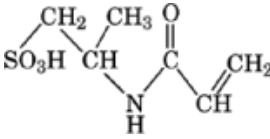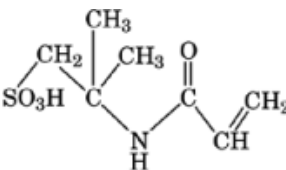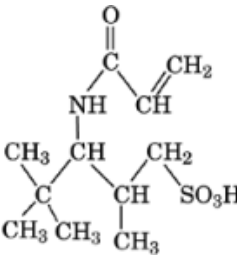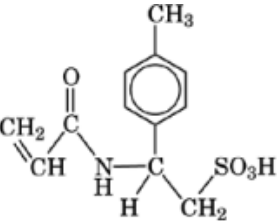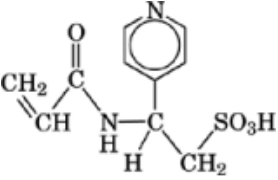
Trifluoromethanesulfonic acid, also known as triflic acid [1493-13-6] is widely used in organic syntheses and has been thoroughly reviewed (93, 94). It was first prepared in 1954 via the oxidation of bis(trifluoromethylthio)mercury with hydrogen peroxide [7722-84-1] (95). Several other routes of preparation have been disclosed (96–98). The acid exhibits excellent thermal and hydrolytic stability, it is not readily oxidized or reduced, nor is it prone to fluoride anion generation.

Trifluoromethanesulfonic acid is used for the polymerization of aromatic olefins (99). Highly branched paraffin hydrocarbons having high octane values can be prepared, using catalytic amounts of trifluoromethanesulfonic acid, via the alkylation of isoparaffin hydrocarbons with olefins for use as fuel additives (100). Catalytic amounts of trifluoromethanesulfonic acid are used to produce hydrocarbon-based oils from phenol [108-95-2] and coal (101). Trifluoromethanesulfonic acid has been widely utilized as a catalyst in Friedel-Crafts alkylation and acylation reactions, as well as a catalyst in organometallic chemistry. Cyclic and straight-chain polyethers are also prepared via the trifluoromethanesulfonic acid-catalyzed polymerization of tetrahydrofuran [109-99-9] (102). Trifluoromethanesulfonic acid is used to produce p-type semiconductors (qv) and various other conducting polymers via the doping of polyacetylene (103–105).

A compound closely related to trifluoromethane sulfonic acid, pentafluoroethanesulfonic acid (pentflic acid), $CF_3CF_2SO_2H$, has also been prepared and utilized as an organic catalyst (106). The material is

Table 5. Alkenylamidoalkanesulfonic Acids

Chemical name	R	CAS Registry Number
2-acrylamidopropanesulfonic acid		[33028-26-1]
2-acrylamido-2-methylpropanesulfonic acid		[15214-89-8]
3-acrylamido-2,4,4-trimethylpentane-sulfonic acid		[79647-72-6]
2-acrylamido-2-(*p*-tolyl)ethanesulfonic acid		[79647-73-7]
2-acrylamido-2-pyridylethanesulfonic acid		[79647-74-8]

generated via the lithiation of CF_3CF_2I, followed by sulfonylation with SO_2, oxidation with H_2O_2, and hydrolysis. Trifluoromethanesulfonic acid can be combined with antimony pentafluoride [7783-70-2] to form Magic Acid, a superacid catalyst. Magic Acid has been used as a catalyst to alkylate benzene and in the hydroisomerization of paraffin-based hydrocarbons for use in motor fuels (107, 108). The superacid catalyst is also utilized in the polymerization of formaldehyde with carbon monoxide (109). One of the most widely used sulfonic acid-based catalysts is Nafion-H [66796-30-3] (**6**), manufactured by E. I. du Pont de Nemours & Co., Inc. It is a perfluorinated ion-exchange polymeric sulfonic acid, available in both the powdered and membrane forms, with a wide variety of commercial catalytic applications (110). This particular polymer is advantageous owing to its inertness to strong acids, strong bases, and reducing and oxidizing agents.

$$+(CF_2CF_2)_n - CF_2 - CF \rightarrow_x$$
$$O(CF_2CF(CF_3)O)_m CF_2CF_2SO_3H$$

(6)
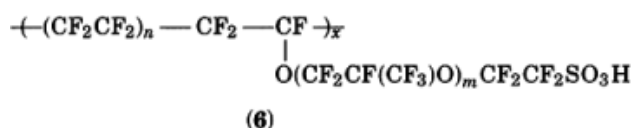
The sulfonic acid moiety has been incorporated into a variety of nonfluorinated polymeric materials (111). Chain-end sulfonated polymers are produced by the reaction of sultones with polymeric organolithiums (112). Polymeric sulfonic acids such as these are incorporated in positive-working photoresist compositions (113).
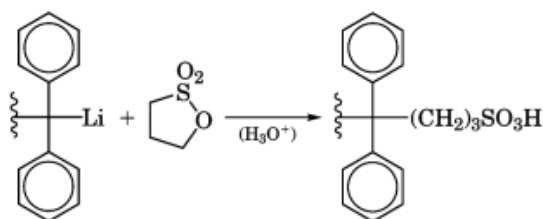

10. Biological Uses

Taurine [107-35-7] (2-aminoethanesulfonic acid), is the only known naturally occurring sulfonic acid. The material is an essential amino acid for cats and is used extensively by Ralston Purina Company as a food supplement in cat food manufacture. Approximately 5,000–6,000 t of taurine (synthetic and natural) were produced in 1993; 50% for pet food manufacture, 50% in pharmaceutical applications (114).

Sulfonic acids have found greatly expanded usage in biological applications. Whereas many of these sulfonic acids are not produced commercially on a large scale, these compounds are important. A review of the biological activity of sulfonic acids has been written (115). Whereas the toxicity of sulfonic acids is in general rather high, several sulfonic acids are beneficially utilized *in vivo*. Taurocholic acid (**7**) is an important bile component, aiding in the digestion of fat (116).

(7)
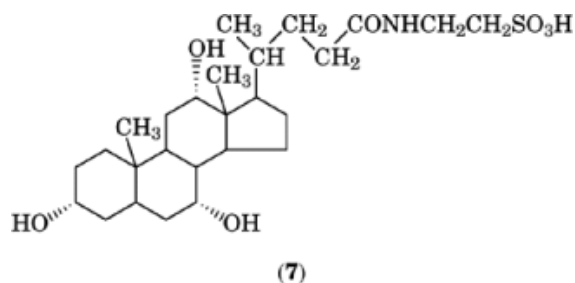
Sulfonic acids are beginning to find widespread, specialized use both *in vitro* and *in vivo*. 8-Anilino-1-naphthalenesulfonic acid [82-76-8] (**8**) is used as a fluorescent probe for the study of proteins (117). Saclofen (3-amino-2-(4-chlorophenyl)propanesulfonic acid) (**9**) is a powerful antagonist of GABA at the GABAB receptor site (118). Potent inhibition of the herpes simplex virus has been observed using biphenyl disulfonic acid urea copolymers (119). Sulfonic acid derivatives have been shown to be potent antihuman immunodeficiency virus (anti-HIV) agents (120, 121) (see Antiviral agents). Sulfonated polystyrene ($_{\text{mol wt}} = 8000$) (**10**) has shown potent HIV-inhibitory properties, without being overly toxic to host cells, during *in vitro* HIV-1 and HIV-2 reverse transcriptase inhibitory activity studies (122, 123). Sulfonic acid-based azo dye derivatives have been patented for HIV treatment, although the use of these materials is limited (124).


(8)

(9)
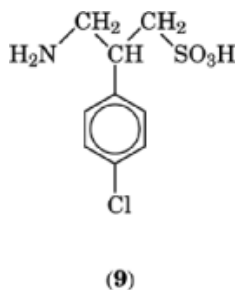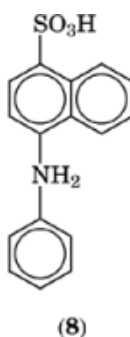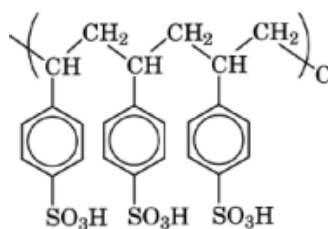
(10)

10.1. Other Applications

Hydroxylamine-*O*-sulfonic acid [2950-43-8] has many applications in the area of organic synthesis. The use of this material for organic transformations has been thoroughly reviewed (125, 126). The preparation of the acid involves the reaction of hydroxylamine [5470-11-1] with oleum in the presence of ammonium sulfate [7783-20-2] (127). The acid has found application in the preparation of hydrazines from amines, aliphatic amines from activated methylene compounds, aromatic amines from activated aromatic compounds, amides from esters, and oximes. It is also an important reagent in reductive deamination and specialty nitrile production.

Two important widely used sulfonic acids are known as Twitchell's reagents, or as in Russia, the Petrov catalysts. These reagents are based on benzene or naphthalene **(11)** and **(12)**, [3055-92-3] and [82415-39-2], respectively. The materials are typically made by the coupling of an unsaturated fatty acid with benzene or naphthalene in the presence of concentrated sulfuric acid (128). These sulfonic acids have been used extensively in the hydrolysis of fats and oils, such as beef tallow (129), coconut oil (130, 131), fatty methyl esters (132), and various other fats and oils (133–135). Twitchell reagents have also found use as acidic esterification catalysts (136) and dispersing agents (137).
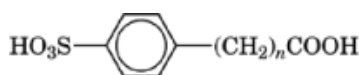
(11)
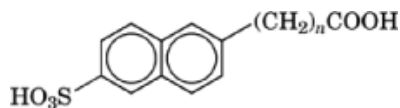
(12)

Petroleum sulfonates have found wide usage in enhanced oil recovery technology (138). This technology involves the sulfonation, often in several steps using several different sulfonating agents, of a petroleum-based feedstock, which contains a wide mixture of aromatics, polycyclic aromatics, and paraffins, to produce a mixture of sulfonic acids which are neutralized to the corresponding sulfonates. The sulfonates are then used in the chemical flooding methods via injection into an existing oil well for enhancing the recovery of oil which is entrained in rock below the surface. These sulfonates can be inexpensively produced and are effective in the desired lowering of surface tension (oil in water) (see Petroleum, enhanced oil recovery).

The uses of methane sulfonic acid are broad (see Sulfur compounds). A variety of barium sulfonates have found use in antifriction lubricants for high speed bearing applications (see Bearing materials) (139). Calcium and sodium salts of sulfonated olefins, esters, or oils are used for the enhancement of extreme pressure properties of grease and gear lubricants (see Lubrication and lubricants) (140, 141). These sulfonic acid salts are

also used as combustion aids for gas oils and fuel oils, and also as detergent–dispersant additives for lubricants (142). Zirconium salts of alkyl and alkylaryl sulfonic acids are used in fuel oils to reduce particulate emissions when the fuel oils are burned (143). Magnesium salts of sulfonic acids are broadly used in lubricating oils to reduce the wear of moving parts (144). The calcium, magnesium, sodium, triethanolamine, and isopropylamine salts of alkylaryl sulfonic acids are useful in oil slick dispersion, especially at low seawater temperatures (145).

Sulfonic acid salts have found widespread use in the area of corrosion inhibition. Lubrizol Corporation produces a wide variety of sulfonic acids, particularly in the form of magnesium salts, for use in lubricant formulations, anticorrosion coatings, greases, and resins (146, 147). Petroleum sulfonates are used in epoxy resin elastomers to improve anticorrosion properties of coatings and sealants (qv) (148, 149).

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