

SULFONATION AND SULFATION

INTRODUCTION:

Sulfonation may be defined as any chemical process by which the **sulfonic acid group** (SO_2OH) or the corresponding salt or sulfonyl halide group (e.g. $-\text{SO}_2\text{Cl}$) is **introduced** into an **organic compound**. These **groups** may be situated **on** either a **carbon** or a **nitrogen** atom. **Sulfonates** of the **second type** (e.g. RNHSO_2ONa) are termed **N-sulfonates** or **sulfamates**.

Particular types of sulfonation include **sulfo-chlorination** (introduction of an $-\text{SO}_2\text{Cl}$ group into an alkane using sulfur dioxide and chlorine), **halo-sulfonation** (reaction of halosulfonic acid $-\text{ClSO}_3\text{H}$ or $-\text{FSO}_3\text{H}$ with an aromatic or heterocyclic compound to introduce an $-\text{SO}_2\text{Cl}$ or an $-\text{SO}_2\text{F}$ group), **sulfoxidation** (use of sulfur dioxide and oxygen to sulfonate an alkane), **sulfo-alkylation**, **sulfo-acylation** and **sulfo-arylation** (introduction of sulfalkyl, sulfoacyl or sulfoaryl groups).

Sulfation involves placement of $-\text{OSO}_2\text{OH}$ group on **carbon** yielding an acid sulfate (ROSO_2OH) or of the $-\text{SO}_4-$ group **between two carbons**, forming the sulfate ROSO_2OR

Sulfato-alkylation designate introduction of a sulfated alkyl group into an organic compound.

CLASSIFICATION OF SULFONATES:

- Aliphatic and alicyclic
- Aromatic
- Heterocyclic and
- N-sulfonates or sulfamates.

The first three types have the $-\text{SO}_2\text{OH}$ group on carbon, the chemical nature of which determines the classification. Thus, $\text{C}_6\text{H}_5\text{OCH}_2\text{SO}_2\text{ONa}$ (sodium-phenoxyethanesulfonate) would be considered an aliphatic sulfonate.

For **practical reasons**, it is also useful to refer to **three other types of sulfonates**, namely those **derived from petroleum fractions**, from **lignin**, and from **fatty oils**. These materials are mixtures of indeterminate or variable composition, probably comprising one or more of the main chemical types of sulfonates together with sulfates and other sulfur compounds, and are made largely by empirical procedures. All three types are commercially important.

CLASSIFICATION OF SULFATES:

Sulfates may be classified as sulfated alkenes, alcohol sulfates, cyclic sulfates, sulfated carbohydrates and sulfated nitrogenous polysaccharides.

GENERAL PROCEDURES FOR PREPARING SULFONATES:

- Treatment of an organic compound with SO₃ or a compound thereof
- Treatment with a compound of SO₂
- Condensation and polymerization methods
- Oxidation of organic compound which already containing sulfur in a lower state of oxidation such as RSH.

Condensation procedures refer to the reaction of organic sulfonates building blocks (such as HOCH₂CH₂SO₃Na) with other organic compounds (such as long-chain acid chlorides) to form new sulfonates with altered properties; these methods include sulfoalkylation, sulfoacylation and sulfoarylation.

For the **preparation of sulfates**, the **first** and **third** (i.e. sulfatoalkylation) methods only are of interest.

SULFONATING AND SULFATING AGENTS AND THEIR PRINCIPAL APPLICATION

Sulfonating and sulfating agents are of two types (1) inorganic and (2) organic. The latter type is employed in the condensation procedures.

Principal sulfonating and sulfating agents

Sulfur trioxide and compounds thereof

- Sulfur trioxide, oleum, concentrated sulfuric acid (SO₃ plus water)
- Chlorosulfonic acid (SO₃ plus HCl)
- Sulfur trioxide adducts with organic compounds
- Sulfamic acid

The sulfur dioxide group

- Sulfurous acid, metallic sulfites
- Sulfur dioxides with chlorine
- Sulfur dioxide with oxygen

Sulfoalkylating agents

- Sulfo-methylating agents (hydroxy and aminomethanesulfonates)
 - Sulfo-ethylating agents (hydroxy-chloro and methylaminoethanesulfonates, ethylenesulfonic acid)
 - Miscellaneous sulfo-alkylating agents, sulfo-acylation, sulfo-arylation, sulfato-alkylation
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Uses and application of sulfonate and sulfates

Millions of tons of **sulfonates** are manufactured annually **lignin sulfonates** obtains as a **by-product** of **paper manufacture** constitutes the major single product. These compounds have achieved a wide variety of interesting and important uses. Most of them are employed as such in acid or salt form for application where the strongly polar hydrophilic -SO₂OH group confers needed properties on a comparatively hydrophobic non-polar organic molecule. A **few sulfonates** are both marketed and used in acid form, including methane and toluenesulfonic acids as catalysts and phenolsulfonic acid as an **electroplating additive**. A considerably larger group is marketed in salt form and used in acid form; such compounds include **mothproofing agents**, and synthetic tanning agents. In these cases, the salts are applied in acid medium, thereby liberating the free -SO₂OH group, which firmly attaches the organic molecule to the textile fiber or leather. The major quantity of **sulfonates and sulfates** is both marketed and used in **salt form**. This **category includes** detergents, emulsifying, deemulsifying, penetrating, wetting and solubilising agents, lubricant additives, and rust inhibitors. Polymeric sulfonates include dispersing agents, elastomers, water-soluble synthetic gums and thickening agents and ion exchange resins which function as strong acids with complete water insolubility and unusual combination of properties leading to many important applications.

Aromatic sulfonyl chlorides -RSO₂Cl are useful for preparing sulfonamides (including sulfa drugs, dyes, tanning agents, plasticizers and the sweetening agents (saccharin) and sulfonate ester (insecticides).

Sulfamates include herbicide, sweetening agent and blood anticoagulant.

Sulfonates and sulfates find use **as intermediates** for preparing organic **compounds not containing sulfur**, notably phenols (prepared by caustic fusion of various sulfonates) and alcohols (made by hydrolysis of sulfated alkenes). Phenol, resorcinol, the naphthols, hydroxy-anthraquinones and 8-hydroxyquinoline are phenols so produced while ethanol and isopropanol are examples of alcohols made from the sulfates.

Factors ensure rapid and complete sulfonation

- use of about **25% excess acid**, corresponding to about 40% excess over that actually converted to sulfonate
 - Distillation of a **quantity of water** (22.2 moles) only **slightly less** than the amount of naphthalene (23.5 moles) sulfonated
 - Use of an **elevated reaction temperature**. At this temperature, water will distill from dilute acid until it has increased to 68% in concentration, which is above the concentration (64%) required to sulfonate naphthalene at this temperature.
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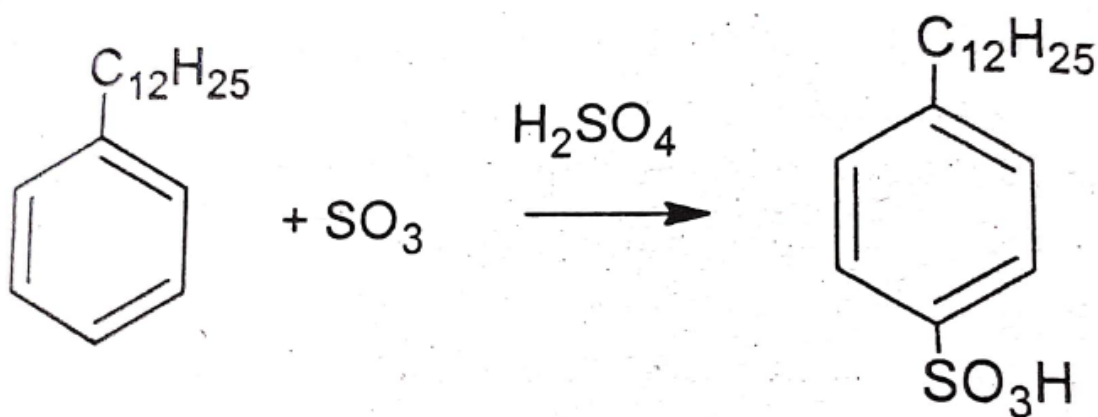
- As in every important sulfonation, **several modified procedures** have been suggested to reduce the acid factor more closely to theoretical, including the use of excess naphthalene or operation under vacuum. Continuous operation has also been studied. None of these expedients has been adopted commercially. Variations in the working up procedure have however sometimes proved advantageous.
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APPLICATIONS:

The sulfonic acids and their derivatives are important industrial chemicals, useful as catalysts, detergents, emulsifying agents, lubricating oil additives, ion exchange resins. They are intermediates for the preparation of phenolic compounds, dyes, pharmaceuticals, tanning agents, pesticides and other products. The use of these compounds depends on the presence of hydrophilic, highly polar sulphonic acid group ($-\text{SO}_2\text{OH}$).

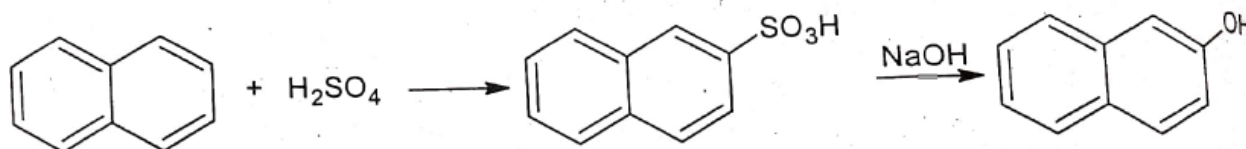
1. Detergents, emulsifying and dispersing agents:

Water soluble sulfonates grouping is combined with an oil soluble organic portion in many ways to produce a variety of desired effects. For example, Long chain alkylbenzenesulfonic acid salts are used in household detergents.



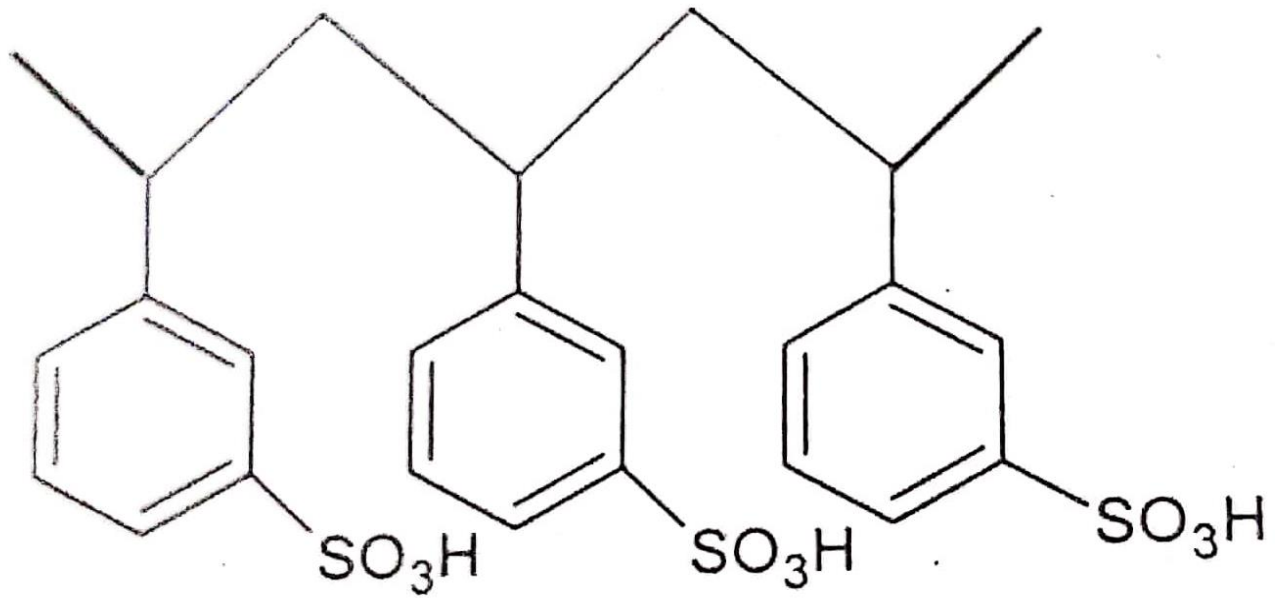
2. Dyes, mothproofing compounds and synthetic tanning agent:

Sulfonic acid group make the compound water soluble and then to attach the organic molecule firmly to fiber or lather.



3. Ion Exchange resins:

They function as strong acids that are completely insoluble in water, an unusual combination of properties leading to many applications.



4. Sweetening and anti-coagulant agent:

Certain sulfamates are used as sweetening agents.

