

Natubhai V. Patel College of Pure & Applied Sciences

T. Y. B.Sc. (Industrial chemistry)

IC – 302: Unit Process, Synthetic dyes and Pharmaceuticals

UNIT – 2A

Syllabus

Sulfonation: Introduction, sulfonating agents, mechanism and commercial manufacturing of benzene sulfonic acid (Barbet process) and Naphthalene sulfonic acid.

SULFONATION AND SULFATION2.0 INTRODUCTION

Sulfonation may be defined as any chemical process by which the **sulfonic acid group (SO₂OH)** or the corresponding salt or sulfonyl halide group (e.g. **-SO₂Cl**) 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. RNHSO₂ONa) are termed **N-sulfonates** or **sulfamates**.

Particular types of sulfonation include **sulfo-chlorination** (introduction of an -SO₂Cl group into an alkane using sulfur dioxide and chlorine), **halo-sulfonation** (reaction of halosulfonic acid —ClSO₃H or —FSO₃H with an aromatic or heterocyclic compound to introduce an —SO₂Cl or an —SO₂F 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 **—OSO₂OH group** on **carbon** yielding an acid sulfate (ROSO₂OH) or of the **-SO₄- group** **between two carbons**, forming the sulfate ROSO₂OR

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

2.1 CLASSIFICATION OF SULFONATES

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

The first three types have the - SO₂OH group on carbon, the chemical nature of which determines the classification. Thus, C₆H₅OCH₂SO₂ONa (sodium-phenoxy methanesulfonate) 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.

2.2 CLASSIFICATION OF SULFATES

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

2.3 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 $\text{HOCH}_2\text{CH}_2\text{SO}_3\text{Na}$) 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.

2.4 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.

2.4.1 Principal sulfonating and sulfating agents

Sulfur trioxide and compounds thereof

- Sulfur trioxide, oleum, concentrated sulfuric acid (SO_3 plus water)
- Chlorosulfonic acid (SO_3 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

2.4.2 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 $-\text{SO}_2\text{OH}$ 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 $-\text{SO}_2\text{OH}$ 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 $-\text{RSO}_2\text{Cl}$ 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.

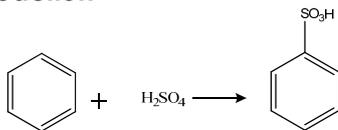
Sulfonates and sulfates find use **as intermediates** for preparing organic **compounds not containing sulfur**, notably phenols (prepared by caustic fusion of various sulfonates) and alcohols (made by hydrolysis of sulfated alkenes). Phenol, resorcinol, the naphthols, hydroxy-anthraquinones and 8-hydroxyquinoline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

2.5 BENZENE SULFONIC ACID OR MONOSULFONATION OF BENZENE

2.5.1 Raw materials

Under **optimum condition**, the **reaction time** for this process has been calculated at **1.5hr. at 180°C** using a seven-stage reactor, continuous process 10 moles of benzene per mole of sulfuric acid required. In contrast, the same process operated in batches at 160-180°C would require 14 hr. and 6-8 moles of benzene per mole sulfuric acid. Thus the continuous method increases by nearly ten times the capacity of the batch method. It is further estimated that the ratio of benzene used, to benzene reacted could be reduced as low as 3 :1 by doubling the time of reaction. The efficiency of the process can be further increased by using 10% oleum instead of sulfuric acid, thereby reducing the required water removal without substantially raising by product sulfone formation.

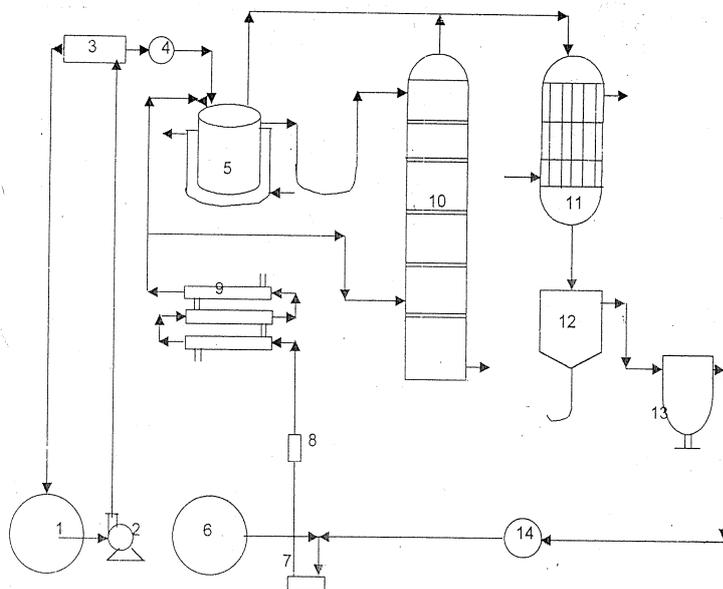
2.5.2 Reaction



2.5.3 Manufacture

Benzene can be monosulfonated efficiently and on a continuous basis by the partial pressure distillation method. A typical operating procedure based on the flow diagram shown in figure is as follow.

Sulfuric acid is continuously pumped from storage tank (1) by means of pump (2) through pressure regulator (3) and meter (4) to the sulfonator (5) **Liquid benzene** from storage tank (6 or 14) is continuously fed by pump (7) through meter (8) to the direct vaporizer super heater (9) and hence to the sulfonator (5) and the Sulfonation tower (10) In the Sulfonation,



1. H₂SO₄ storage tank
2. Pump
3. Pressure regulator
4. Flow-meter
5. Sulfonator
6. Liquid benzene storage tank
7. Pump
8. Meter
9. Vaporizer
10. Sulfonation tower
11. Condensor
12. Separator
13. Neutralizing drier
14. Liquid benzene storage tank

Sulfuric acid reacts with **benzene**, and the **reaction mass** containing **30%** un-reacted sulfuric acid flows out continuously to the top of the Sulfonation tower (10) which is arranged like a plate column, the reaction mass flows downward through the tower while further reacting with a **countercurrent stream** of benzene vapour.

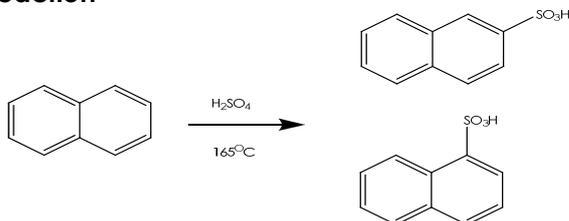
The exit benzene-water vapour are continuously discharged from top of tower (10) to condenser (11) and stratified in separator (12) and the benzene storage (14) while the benzenesulfonic acid, containing **2.5-3.5%** of sulfone and **3-4%** of sulfuric acid is continuously drawn off at the bottom of the tower.

2.6 NAPHTHALINE β - SULFONIC ACID

2.6.1 Raw materials

Naphthalene, sulfuric acid, water, steam etc

2.6.2 Reaction



2.7.3 Manufacture

The hydrocarbon is reacted with sulfuric acid; in addition to the desired isomer, about 15% of the alpha isomer is also formed.

Naphthalene (3,350 lb - 26.2 lb moles) is charged to a **cast iron sulfonation kettle**, 500 gal capacity, equipped with propeller or anchor agitator and heated either directly with generator gas or by **high-pressure** (100 lb) jacket steam. It is melted by heating to **90-110 °C**. **Sulfuric acid** (3,350 lb of 96% strength - 32.8 lb moles) is then added with agitation, the temperature being allowed to rise to about **160 °C**. The batch is held at **160 -165°C** for about **2hrs** to complete reaction, during which time **water** (approx. 400 lb-22.2 lb moles) and **naphthalene** (approx. 350 lb -2.7 lb moles) distill off and are collected by condensation. The reaction **products contains** mainly monosulfonic acids (85 % beta and 15% alphas) plus some **sulfone**, free sulfuric acid, disulfonic acids and tar. The **undesired α - sulfonate** is now removed by blowing **dry steam** into the charge to effect **hydrolytic desulfonation**, the liberated naphthalene being distilled and recovered. It is essential to employ dry steam to avoid foaming and to maintain a temperature in the range **160-165°C** to ensure rapid reaction. About **16% or 540 lb** of the original naphthalene employed is recovered, leaving the **β -sulfonate** contaminated with only about 0.1% alpha isomer.

The **hydrolyzed** sulfonation mixture is discharged into the water with good agitation and the resulting solution is run into the brine to form the sodium sulfonate salt. The **slurry** so obtained is **agitated** for **10 hr** as it **cooled to 30 °C** this yields an easily **filterable precipitate**. The filtration is accomplished by pumping or blowing the sodium sulfonate suspension into a pressure filter containing wooden plate filters and rubber-coated frames. The shell of the filter is coated with tar to minimize corrosion. The filtrate is permit to stand and more salt added if necessary and then it is refiltered to collect any additional sulfonate that has crystallized out.

The **second crop** of sodium sulfonate is not as pure as the first. The filter cakes are washed with a minimum of water and these washings are employed to advantage as part of the liquor in the sulfonation dilution tank. The filter cake of sodium sulfonate containing about 70 % water is pressed hydraulically to a water content of about 30%. The press cakes are dried to moisture content of about 5%, disintegrated and delivered to the **caustic fusion kettles** for conversion to **β -naphthol**. The **yield** is about **90%** of theory on the basis of naphthalene consumed.

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.
- 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.