

SOME DERIVATIVES OF LONG-CHAIN ALIPHATIC CARBOXYLIC ACIDS

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Oils and fats are important not only as food and consumption material but also an indispensable raw material for chemical industry. They are used mainly in the manufacturing of varnishes, paints and surface active agents (Tensides). In many cases fats are cleaved into glycerine and fatty acids before their use. The fatty acids are distilled and are used as a source for very important intermediates. Fatty acid methyl esters are also used as intermediates.

Fatty acids are consumed by vegetable oil industry and on a big scale by detergent industry. So fat industry has developed into a medium sized chemical industry. These industries are comparatively old branches of chemical manufactures and about 100 years ago they were of a remarkable size when other industries were not very well developed. Since a very long time soaps are considered to be of commercial value. Because of lack of supply of raw material, these industries (soap factories, oil mills and fatty acid plants) could not be developed as a main chemical industry. As we know, presently the raw material output of natural fat and oil, which was formerly only raw material for the industry is not having rapid growth.

Therefore the trend of using petroleum as raw material (for example oxidation of wax) has been on an increasing scale. Still the demand of natural oils and fats yet very high.

The annual world production is 10 to 30 million tons, approximately 10 million tons are used for industrial purposes and about 70% are used for human consumption [1]. There is no doubt that a number of important products which serve as raw material substances for the production of foods and semi-luxurious foods can be obtained from basic

natural fats like partial glyceride and diacetyl tartaric ester or citric ester and are also used as emulsifiers extensively. The world production of fats mentioned above also consists of some % of fats, such as castor oil, tung oil, oit-icica oil, linseed oil and so on, which for physiological reasons, are not suitable for human consumption [2]. The same is the case for waste fat from knackery and slaughter houses and from bone extractions which are used for industrial purposes exclusively. In addition, we must remember here about "Refining of fatty acids". Preparation of surface active agents from fatty acids as basic materials is the central point of this paper.

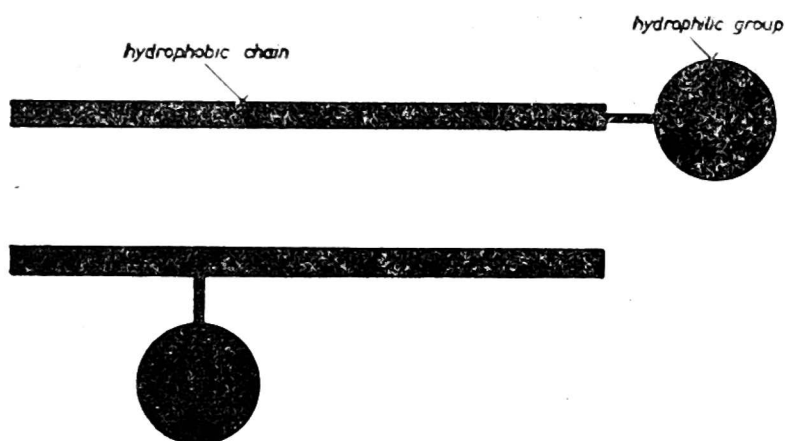


Fig. 1. Characteristic criterion of surface active agents with unbranched hydrophobic chain

The ability to adsorb on interface between liquid and gas, which means water and air, is the criterion for the measurement of surface activity.

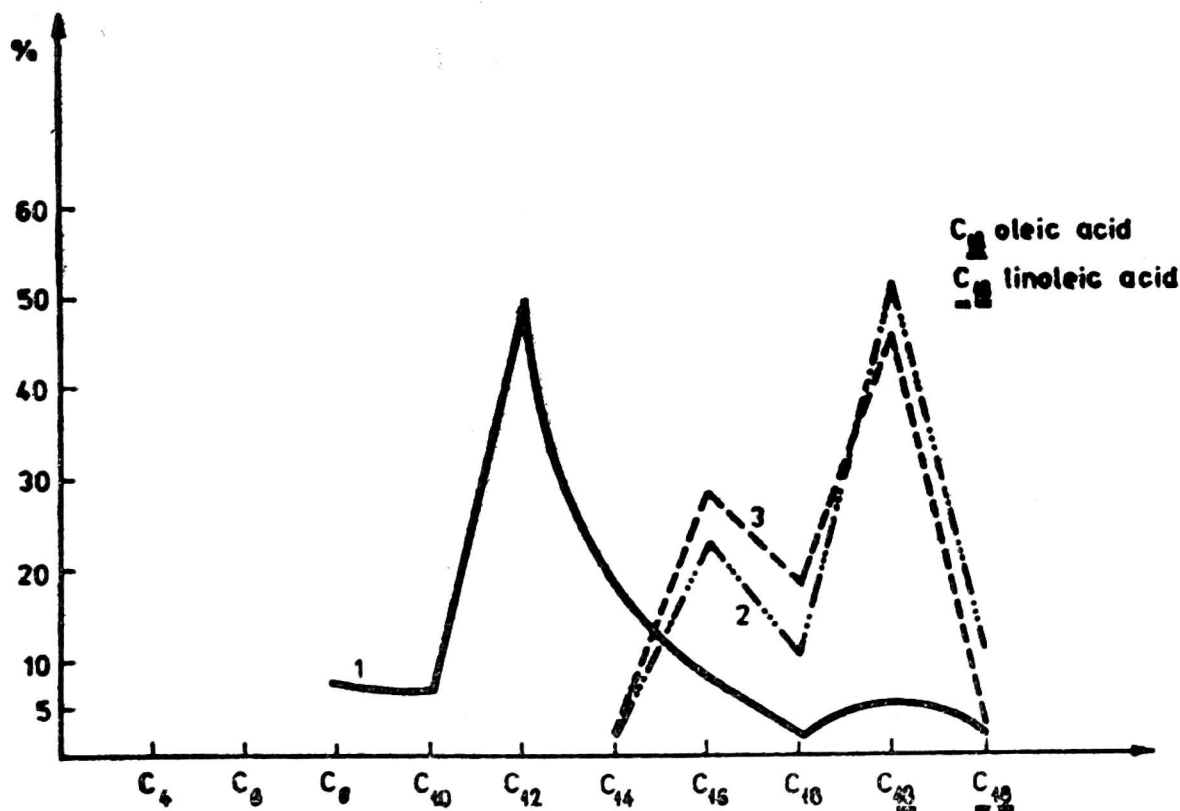


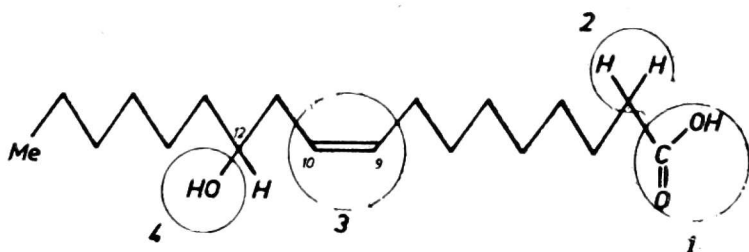
Fig. 2. Average composition of coconut oil, tallow and lard

The hydrophobic part is contained in fatty acids. In soaps we find both hydrophobic and hydrophilic parts. Therefore soaps are the oldest surfactants.

Properties of surfactants depend on the composition of the basic fat.

Suitable is a carbon chain length C_{12} - C_{14} . Therefore, for example, there is a difference in properties between surfactants obtained from animal fat and coconut fat. The properties differ in water solubility and action on interface. That is why we cannot replace coconut fat by animal fat. All existing experiments to replace coconut fatty acids by animal fatty acids have not been successful. The reason is that the composition of animal fats which are in contrast to coconut fat contain only small quantities of lauric and myristic acid glycerides.

Fig. 3. Places of introducing a hydrophylic group in a ricinoleic acid



Principles of introducing a hydrophilic group in a fatty acid molecule:

- 1) reaction of the carboxylic group,
- 2) replacement reactions of hydrogen atom, especially in the α -position near the carboxylic group,
- 3) reaction of the double bond,
- 4) reaction of the hydroxylic group, and
- 5) competitive reactions on these reactive centres with view to study the dependency of the properties on the modification of the chemical structure of molecule.

REACTION OF THE CARBOXYLIC GROUP

A number of derivatives can be obtained by the reaction with the carboxylic group of straight chain fatty acids. These derivatives are important for the production of detergents, plastics and lubricants. Soaps are obtained simply by mixing them with bases.

SALTS

The most important common soaps are sodium and potassium salts of long chain carboxylic acids with 12 to 18 carbon atoms (laundry soaps and soft soaps).

The production of soaps from fat and lye with ashes and their use as medicinal and cleaning agents have already been reported in second



Fig. 4. Salts of long chain carboxylic acids. Tensides or initial stages for tensides

century. Also Gauls and Germans were knowing about the soaps. They were using tallow and wood ash for soap-production. Since then we have made great progress in production and application of soaps. Nowadays a number of soaps are available like metal soaps which are partially oil soluble and are used as lubricants, dried oils, pharmaceutical and cosmetic soaps etc. For example zinc ricinoleate is added as deodorant [3].

Trials for changing the chemical properties of soaps have not been much successful. Till now soaps are salts of long chain carboxylic acids which have some advantages over other surfactants but also have some remarkable disadvantages.

Advantages. They are cheap, they good wetting property and emulsification-ability and fatcharacter (solf handle with textile). The classical soaps in soft water never gave great trouble. The micro organisms in the waste water ensured biological purification by means of a ready degradation and elimination of the organic chains.

Disadvantages. Soaps show little resistance against acids and hardbinders (lime soaps); 1/3 is lost. Investigation on dependence of properties of soaps on the structure [3] pointed out that there is dependence on hydrophobic part (shift of CMC). Due to the presence of double bond, the hydrophobic part of molecules becomes apparently shorter so that the surface activity is lowered (sodium palmitate, potassium oleate). Trans configuration decreases the surface activity and solubility of the soaps in contrary to cis compounds and saturated molecules. In presence of OH-group in the chain, solubility is increased (for example ricinoleate).

So products with better properties are yet beting searched sulfonated or sulfated oils. From Turkey red dyeing one process has been developed. Fats and oils are dissolved by the action of sulfuric acid and a product is obtained which is more resistant to hard water and used in textile industry. This process is about 140 years old [4]. However the surface activity of ths product is essentially lower than that of soaps. So this product as Turkey red oil as well as high sulfonated or sulfated oils is used as auxiliary in textile and not as washing material. The first pro-

duct with more suitable properties than of soaps is obtained by the blocking up of carboxyl group in long chain carboxylic acids.

The production of washing agents on the base of synthetic material developed in the second quarter of this century will not be discussed here.

Here I shall report only about fatty acid derivatives as wetting agents, detergents, emulsifiers etc. which are produced in a big industrial scale and are in great demand. Modern processes will be regarded especially

ESTER

Important use of long chain alkyl esters of carboxylic acids is as feed material for α -sulfo fatty acid esters. The solubility in water is also improved by introducing polyhydroxy compounds (esterification with glycerine or sugars). The initial derivatives of polyhydroxy compounds used as surfactants, are fatty acid monoglycerides and fatty acid diglycerides.

Nowadays glycerine fatty acid esters are mostly used as emulsifiers in cosmetics, food, in plastics as plastisizers and in laquers industries [5].

GMFAE are different from GDFAE. Actually GMFAE is a mixture of mono, di and triglycerides. GMFAE have higher surface activity than GDFAE (more OH-groups).

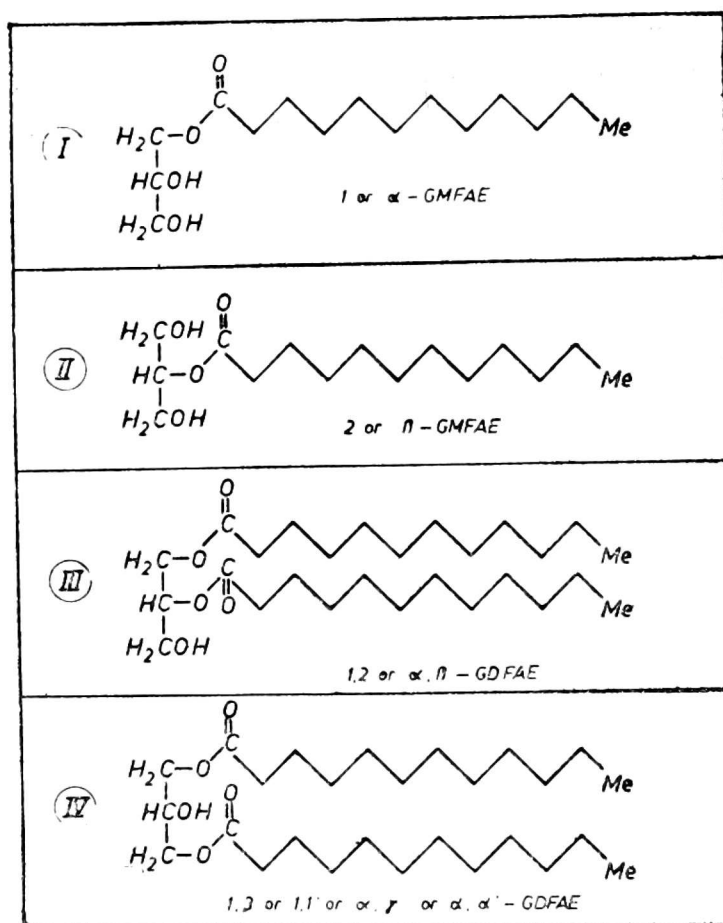


Fig. 5. Glycerol fatty acid esters

Several methods have been described for the production of GMFAE and GDFAE. So called "monoglyceride" is practically a mixture of 40-50% of monoglyceride and the same proportion of diglyceride and small amount of triglyceride. By adding 1-10% of monoglycerides washing material produced by spray-drying can be made without dust. To prevent the formation of dust or lump in spray-dried household detergent product glycerine mono-stearate sulfate as well as the ammonium salt are added. Also in such powdered soaps 5-30% of sodium glycerine mono fatty acid ester sulfate can be added.

Sulfated monoglycerides of fatty acids commercially known as "Syn-tex" detergents are relatively unstable in hot acids and alkalies. A similar type of ester having sulfonate group instead of sulfate, linked to the hydrophobic monoglyceride was firstly patented in about 1960 [6].

Fatty acid monoglycerides are considered as precursors for the production of Fatty acid sugar esters (FASE). As we have seen two hydroxy groups in fatty acid monoglycerides are not sufficient to make hydrophobic hydrocarbon chain water soluble. It was necessary to introduce sulfate or sulfonate group. The same effects can be obtained by introducing a pile of hydroxy groups for example by reaction with sugars which are typical polyhydroxy compounds.

Such fatty acid sugar esters have successfully been produced in the last 20 years by using special solvents in systematic and scientific way. Fatty acid esters from carbohydrates, well known types are mono and trifatty acid esters of sorbit and their anhydrides, were developed by the Atlas Powder Co under the trade mark "Span" and were used as water in oil emulsifiers.

Products obtained from the reaction of ethylene oxide and these esters (trade mark "Tween") are very high soluble in water. They can be used as washing material but they find a major roll as oil in water emulsifiers. In the same way fatty acid esters of pentaerythrite which are available in market as well as their ethylene oxide addition products have the same emulsifying effect. After second world war, in many countries sugar became surplus. This gave an opportunity to react sugar with fat and to use it not only as food but also as raw material for chemical industry. Many countries have undertaken the development of this special branch of surfactants like Sugar Research Foundation, the Berkeley Chemical Corporation, both in United States of America, the Ledoga S.p.A. in Italy, the Howards of Ilford Ltd., England, the Soc. de Produits Chimiques et de Synthèse and the Compagnie Francaise Produits Industrial, France, and the Nippon Sugars, Japan. Also there is a number of research groups in Czechoslovakia,

USSR, Poland and German Democratic Republic working on problems related sugar-surfactants [7-9].

Esters of sucrose having one or two groups of unsaturated and saturated fatty acids are of special interest. Sugar should be specially obtained in very high purity. However in early fifties cane sugar was cheaper than other raw materials for nonionic surfactants like sorbite and ethylene oxide. But in the last few years world sugar price has increased exorbitantly. So the present tendency to use such surfactants is not encouraging.

Mono fatty acid esters of sucrose show the properties depending upon the chain length of the fatty acids and are more or less good soluble in water and show surface activity to reduce interfacial and surface tension of water solutions, show wetting properties, foam and washing power. In contrary difatty soluble in mineral oils, fats and oils and give a good dispersion ability.

A special quality of fatty acid sugar esters is their physiological and-biological behavior. The feed material for these esters are recovered by hydrolysis and some parts from these products are useful as food material. The fatty acid sugar esters are not at all toxic and are in great demand because their good biodegradability.

In early fifties after the development of plastic industry, new solvents like dimethylformamide, dimethylsulfoxide and others were available and also synthesis of partial esters of sucrose was discovered. In the meantime the production of fatty acid sugar esters was developed extensively. The successful method for formation of fatty acid sugar esters was introduced on industrial scale. Specific properties of sucrose must be considered:

- I. Sucrose is sensitive to acids and alkalies,
- II. Temperature sensitivity (above 100°C), and
- III. Sucrose is not soluble in usual organic solvents.

Transesterification is the most successful method for production of fatty acid partial esters of sucrose.

Final product depends upon molar ratio of reactants and reaction time. By changing the molar ratio more monoester or more diester can be obtained. Sucrose esters have many desired properties but they are saponified easily. Therefore it was necessary to obtain sucrose derivatives which have properties of fatty acid esters and which are unhydrolyzable. It was reached successfully in the fifties by reaction of sucrose as well as other sugars and long chain isocyanates [9]. Preparation and purification is similar to the sugar esters. You can obtain sucrose carbamin acid esters without using of alkyl isocyanates by reaction of sucrose,

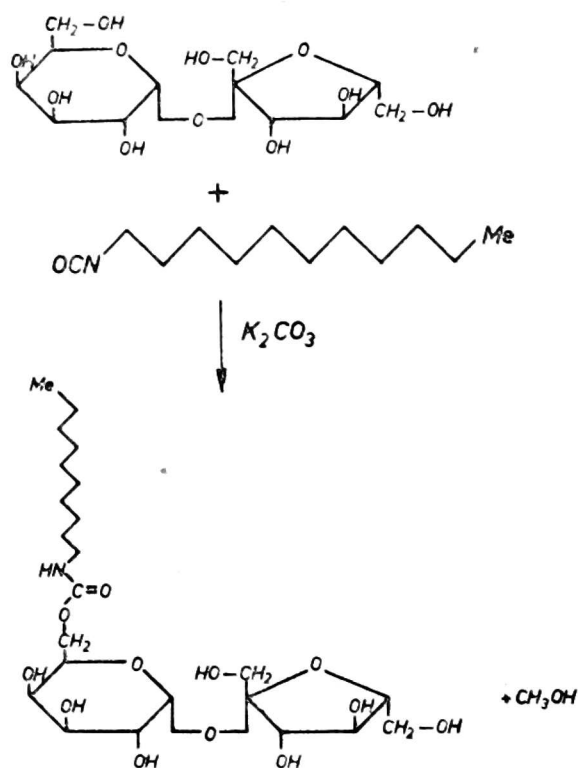
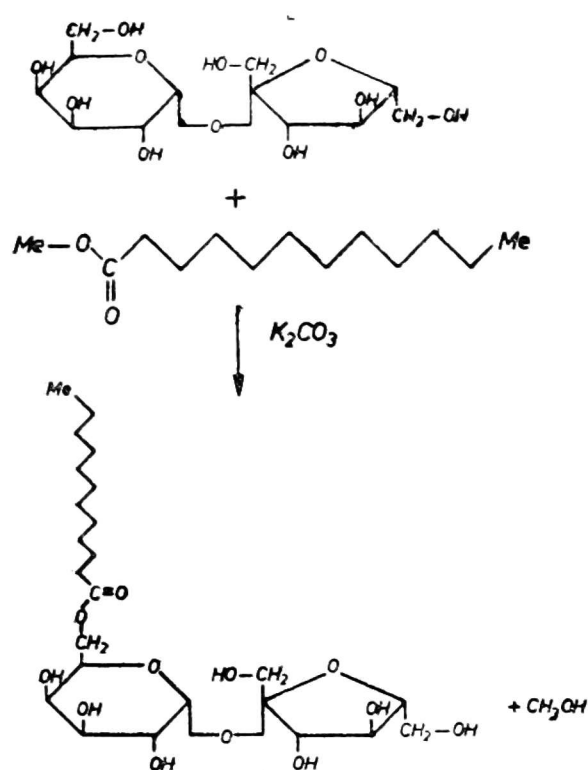


Fig. 6. Classical synthesis of sucrose fatty acid esters

Fig. 7. Sucrose alkyl carbamate acid ester

potassium eynate and alkyl halide in DMF. Yield is about 70-80% of theory [10-13].

The sucrose alkyl carbamate acid esters with a long chain from C₁₆ to C₁₈ are only somewhat soluble in water. Therefore they have been reacted with ethylene oxide.

We suppose that in future use of sugar detergents will be decreased as washing agents. However their use in food industry, cosmetics, pharmaceutical industry, medicinal industry and other specialty chemicals will be increased because of physiological and physical properties. Economy is the decisive factor for the development of this field. The use of DMF as solvent is the main disadvantage in the synthesis. While DMF is used as solvent, it is necessary to purify the product and this makes the product costly.

Products from the reaction of ethylene oxide and fatty acids, polymerhomologs mixtures, are already available in the market on industrial scale [14, 15]. Properties of product depends on the number of ethylenoxide molecules present. As number of ethylene oxide molecules is increased, properties are changed from emulsifiers to wetting agents and washing agents.

The basic chemical reactions for the preparation of the straight-chain fatty acid esters of polyethylene glycol are: there are various applications of oxyethylated fatty acid products. Besides the fatty acids a number of natural fats and oils have been oxyethylated. The use of castor

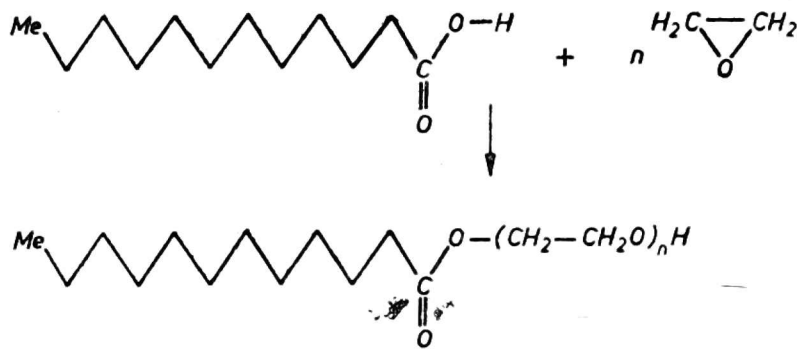


Fig. 8. Reaction fatty acids with ethylene oxide

oil as base for oxyethylation is worth mention. The initial obvious sites for oxyethylation are the hydroxyl groups in the ricinoleic acid chain. The ester groups under the influence of heat, alkaline catalyst, and water traces may provide additional, sites leading to oxyethylated acids, oxyethylated partial glycerides, and even to an insertion of a polyether chain into the glyceride linkage.

NITROGEN DERIVATIVES

The main raw material is tallow and coconut oil. In addition, there are many miscellaneous raw materials used. Among them are soybean oil, cottonseed oil, tall oil fractions, fish oil fractions, erucic acid, and various fat by-products.

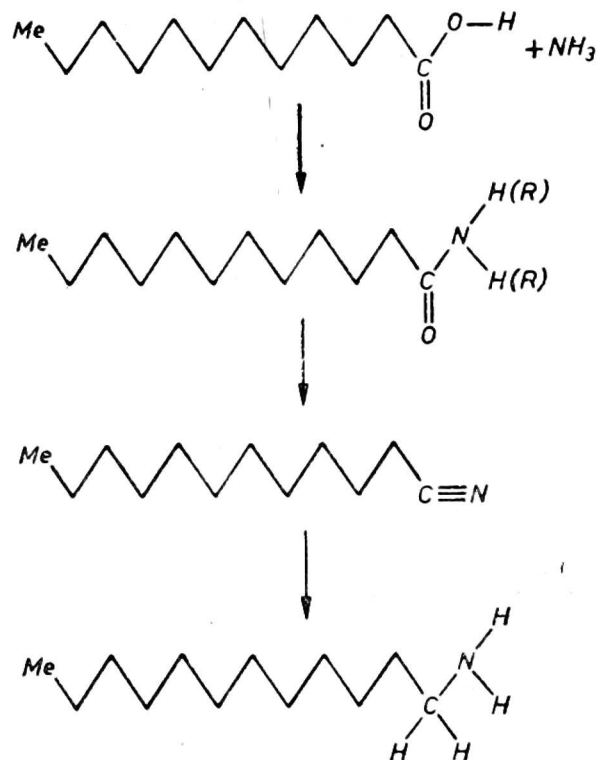


Fig. 9. Nitrogen derivatives of fatty acids

The main procedure is the reaction of fatty acid with ammonia. The first reaction product, after soap preparation, is a simple unsubstituted amide [16]. The reaction is conducted at about 200°C and the yield of amide can be as high as 98%. This amide is sold in large quantities for a variety of uses. It is a hard waxy, high melting material and can be an excellent lubricant. It is also an intermediate in the production of other derivatives.

The substituted amides that could be prepared by the reaction of fatty acids with amines are many in number. Fatty amides can be reacted with almost any primary or secondary amine to produce substituted amides.

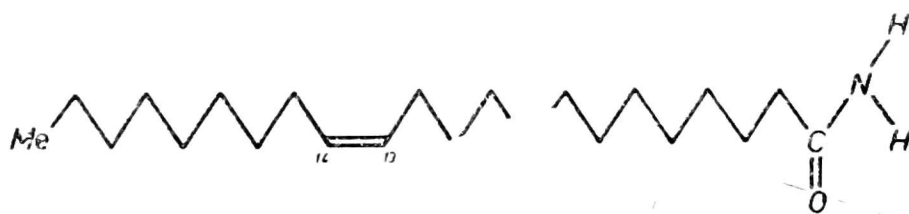


Fig. 10. Erucis acid amide

Erucamides principal use is as an additive to alter the physical characteristics of polyethylene, polypropylene and other polymeres. This type of product is used as a ship additive, an antiblock agent, and for paper coating compositions and water-proofing [17].

Probably the most important of these amidation reactions of fatty acids is the production of the surfactants by the reaction of fatty acids with ethanolamine or diethanolamine [18-22].

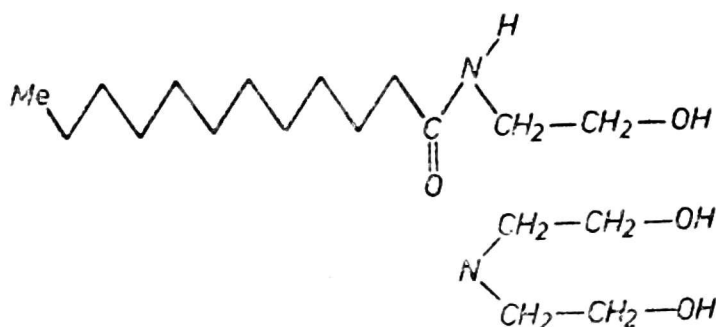


Fig. 11. Fatty acid alkanolamides

Fatty acid alkylol-amides, firstly produced in 1937, have found a versatile application in modern detergents.

It was necessary to fill up a gap between soaps (which are incompatible on special conditions) and synthetic detergents.

By neutralization of fatty acids with mono-, di- or triethanol amine so called "mild" soaps are obtained. These types of soaps are used for hairwashing and shaving creams, also as emulsifiers, and odorants in cosmetics.

By heating in presence of basic catalyts alcanolamides are obtained. Solid, pasty and liquid products can be used. Mono alkyloamides are mainly used for washing powders, whereas in liquid products dialkylol-amides are applied. They are mostly used oas cleaning agents for domestic purposes (diswashing agent, washing powder, shampoo). There is no other group of substances which can be applied as numerous in detergent mixtures. They are also used as emulsifiers for cosmetics or as solvent for fluorescein-coloring matter in lipsticks.

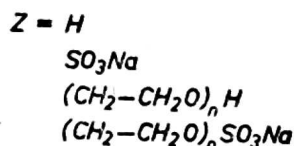
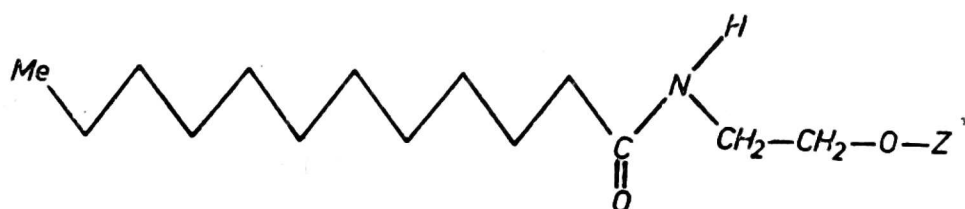


Fig. 12. Mono ethanol amides

Fatty acid ethanol amides are obtained in wax to crystalline form depending on the purity of fatty acids which are used, and melting point is about $40^{\circ}C$ higher than the fatty acids. They are soluble in water only little but due to their special structure, they can be linked with other compounds, for example undecene-(10)-acid mono ethanol amide which is not soluble in water but is good dispersable and solubilisable. So this compound is used as foot-spray due to fungicidic and bactericidic properties.

Mono alkyol amides of lauric and myristic acid are added in cleaning powders to increase foaming power. Products from sulfuric acid and phosphoric acids are good anionics which however are not preferred as alkyl sulfates.

One can differentiate between two types of dialkylol amides: Complex dialkyloamide (reaction with 2-3 mol diethanol amin) and super amide. Both are in good combination with synthetic detergents, nonionics and soaps.

Ethylene oxide adducts have remarkable wetting power. They are effective emulsifiers and wool washers. Ethylene oxide derivatives of

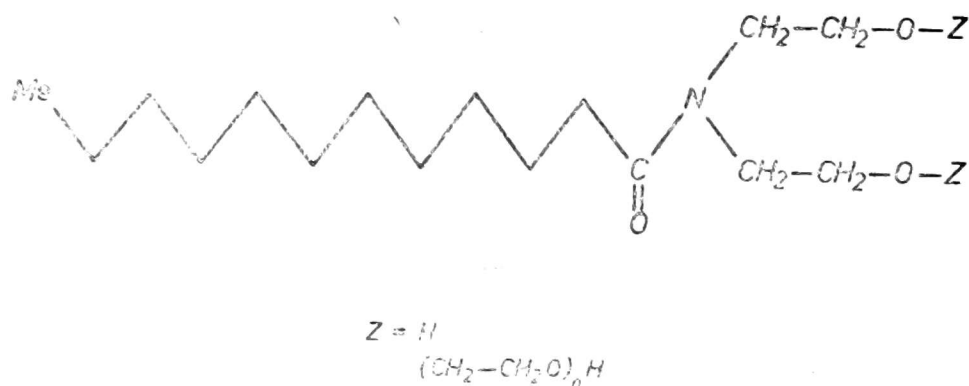


Fig. 13. Diethanol amides

mono-alkylol-amides have not far been used as strongly as ethylene oxide derivatives of dialkylol-amides.

Of considerable commercial significance still, is the reaction product of fatty acid chlorides with N-methyl taurine. This reaction is conducted in a typical Schotten-Baumann-method [23].

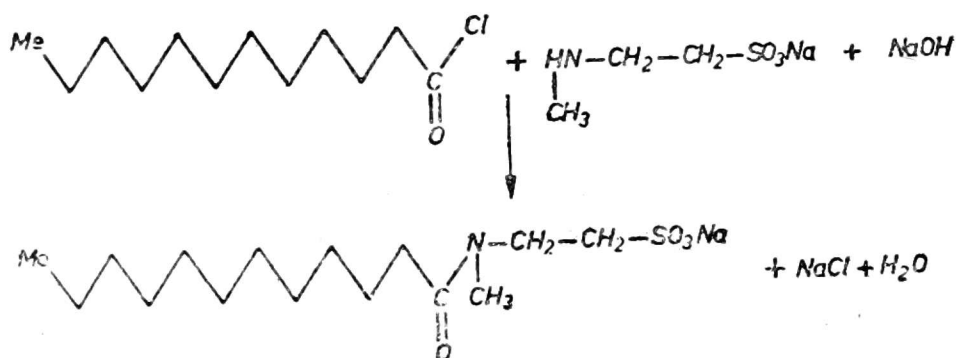


Fig. 14. Schotten-Baumann reaction

These products are, of course, the "Igepons" and have wide uses in the detergent field. Also "Lamepons" condensation products from oleic acid chloride and glutine hydrolysis material are versatile surface active agents. Fat protein condensates are used as household detergent, dispersing agent, and fibre protecting agent.

While nitriles in themselves are not very important commercially, they do serve the important function in that they are intermediates in the production of fatty amines. The largest amount of fatty amines produced find their ultimate disposition in the preparation of "quaternary ammonium compounds". This term is applied to organic nitrogen compounds wherein the four alkyl groups are attached to the nitrogen atom through covalent bonds. Exceptions to this statement will be found in the heterocyclic nitrogen compounds wherein one of the alkyl groups may be replaced by a carbon-nitrogen double bond.

Quaternary ammonium salts are prepared by the exhaustive alkylation of amines. By far the most important of these types are produced by the reaction of amines with methyl chloride.

The starting amine may be primary, secondary, or tertiary. Several alkylating agents are used commercially; among them are methyl sulfate, benzyl chloride, and alkyl halides.

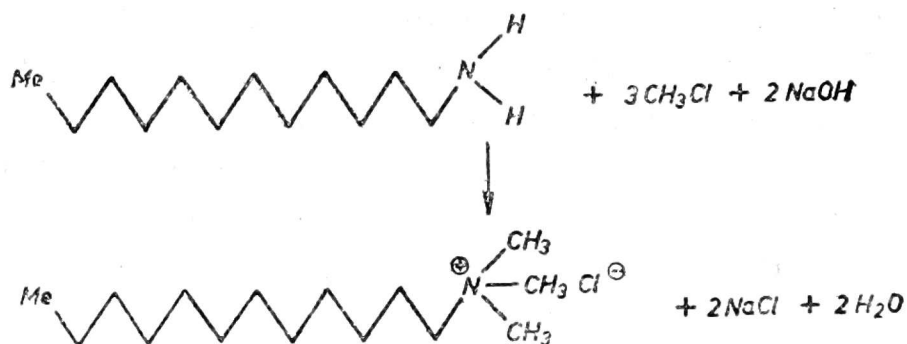


Fig. 15. Quaternary ammonium salts from fatty amines

The quaternary ammonium compounds that contain one long chain alkyl group are water soluble and highly biologically active [24]. The compounds containing two long chains are not water soluble, but are water dispersible. The largest use of this class of materials is in the home laundry softening field. The cationic quaternaries are substantive

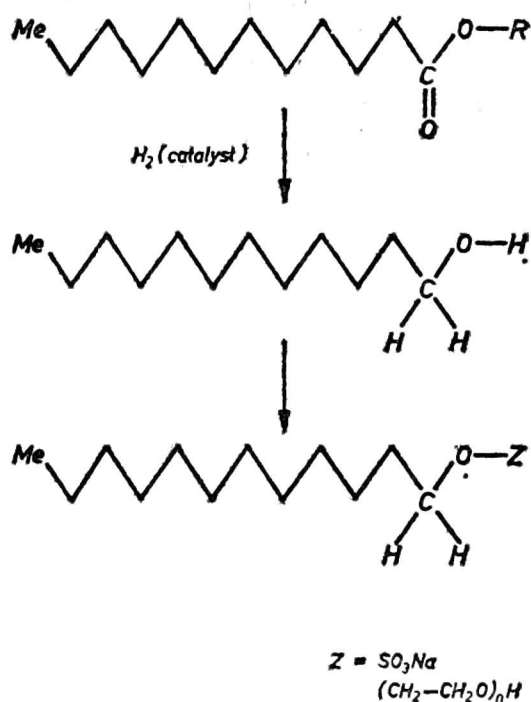


Fig. 16. Transformation of acid alkyl esters into surface active agents

to cotton and impart a soft "hand" to treated goods. Dimethyl dihydrogenated tallow ammonium chloride (or methyl sulfate) is used almost exclusively.

ALCOHOLS

Carboxyl group can be reduced completely to get alcohol. For the synthesis of detergents important alcohols are got by transesterification of glycerides with methanol and hydrogenation of the methyl esters. Sulfated alcohols are lightly biodegradable and oxyethylated alcohols possess significant foam-depressing properties.

Both types of detergents afford important products for the preparation of washing and cleaning agents and are produced on an industrial scale since several decades. Also sulfates which are obtained from the reaction of ethylene oxide and alcohols and subsequent sulfation of the recovered polyether, are compounds with good detergents and lime soap-dispersing properties.

REPLACEMENT REACTIONS OF THE HYDROGEN ATOM, ESPECIALLY IN THE α -POSITION NEAR THE CARBOXYLIC GROUP

On reaction of saturated fatty acids with chlorine, chlorination takes place along the entire chain length. It is not possible to fractionate the mixture of mono- and polychlorinated products. Other methods like reaction of fatty acid esters and bromine in the mixture of acid chlorides yield selective mono-bromination under suitable reaction conditions.

The exchange of halogen with amino group is performed through ammonia. It also can be performed by the reaction of ethylene oxide with amino group and the products, nonionic detergents, have very good industrial properties. Carboxylic groups are introduced through sodium malonic ester or by reaction with sodium cyanide and afterwards their nitrile saponification.

The exchange of halogen group is done by sodium hydrogen carbonate or by other bases. Hydroxy acids lead itself to reactions that will be reported later on. Commercially the most important reaction of the hydrocarbon chain in view of the production of surface active agents is the fixing of sulfonate group. Sulfo acids and esters are used in industry extensively. For many years, sulfo fatty acids have been used in the chemical industry for active washing substances. The use of their compounds and derivatives has been extended in the course of the last years [25-34]. First, they were reported in the nineteen-thirties. In fifties sulfonation of fatty acids and afterwards their esters were inve-

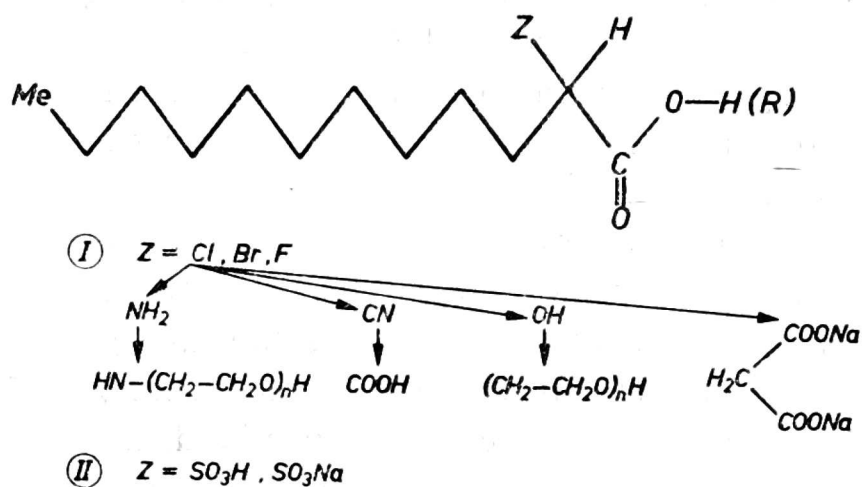


Fig. 17. Reaction of the hydrogen atom especially in the α — position near the carboxylic group

stigated. Up to early sixties there was no easy economical method for the production of these types of compounds on industrial scale. Therefore ester sulfonates were not of practical importance. In the meantime drastic conditions of sulfonation were applied successfully (with SO_3 because of low mobility of H-Atom). It was concluded that side reac-

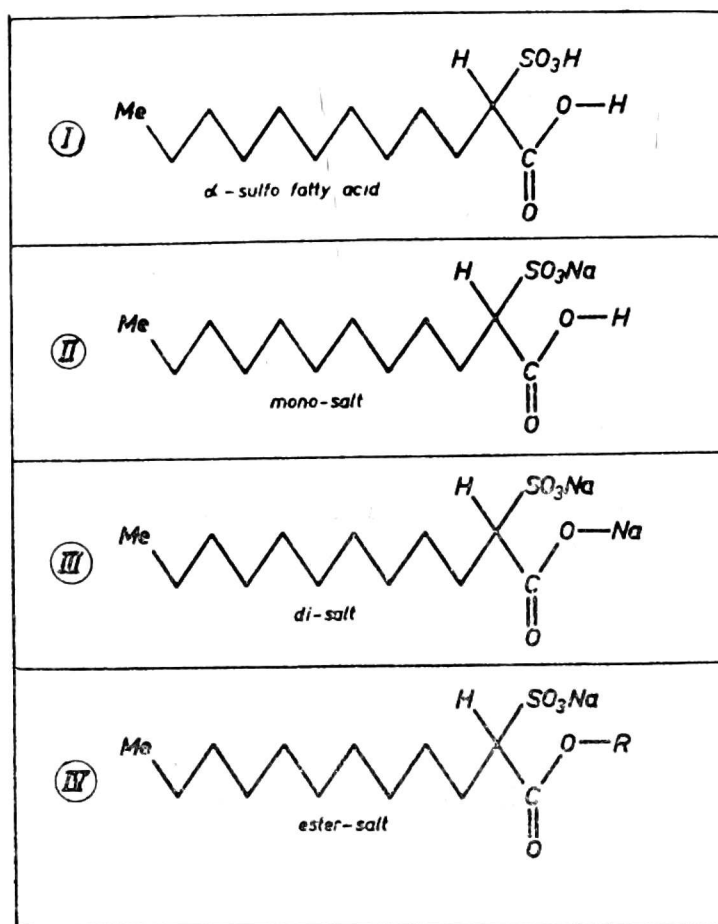


Fig. 18. Types of α -sulfo fatty acids and esters

tions from local heating and excess of SO_3 would give dark-coloured products and this should be avoided (sulfonation with SO_3 gas in mixture of inert-gas preferred, ca. 5 Vol % SO_3 in air at $70\text{--}90^\circ\text{C}$; with discontinuous process 10-22% SO_3 excess; reaction time: 10-20', i.e. with short-time reactor a soft reaction step is necessary).

Fatty acid esters of alcohols with 1-3 carbon atoms are suitable for direct sulfonation. For commercial reasons methyl esters from fatty acid charges of palm oil, coconut oil and tallow are preferred materials.

It is also possible to sulfonate fatty acids directly if 10-25% by wt of fatty acid ester short chain alcohols are added. By combination of 3 steps of the process — sulfonation, bleaching and neutralization — ester sulfonates of good qualities, with a yield of 97% are produced on industrial scale by continuous process.

Sulfonated fatty acids can be produced by two ways:

- I. Sulfonation of fatty acids, and
- II. Hydrolysis of α -sulfonated fatty acid esters.

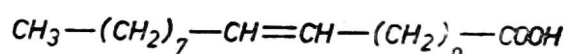
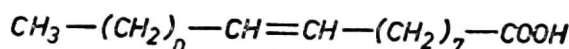


Fig. 19. The series of monoenoic fatty acids

Ester sulfonates and fatty acid sulfonates are of interest not only as detergents but also for cosmetics, auxiliary products for fabrics manufacture, plastics (emulsifiers), rubber (separating agents) and leather finishing due to their special properties: very little toxicity and good skin tolerance.

REACTIONS OF THE DOUBLE BOND

Oleic acid is one of the most important animal fatty acids. Since the end of the last century it is being used as feed material for textile auxiliary materials (sulfuration). We can derive two homologous series from oleic acid by shortening or lengthening the alkyl chain or the moiety with the carboxylic group, and we see that most natural monoenoic acids can be classified in one of the two series [35].

Following reactions on double bond are very important in detergent industry:

- I. Addition of bisulfite or $\text{SO}_3 \rightarrow$ sulfonic acids,
- II. Addition of halogen \rightarrow dihalogen ated fatty acids,
- III. Addition of $\text{HX} \rightarrow$ monohalogen ated fatty acids,

- IV. Addition of $\text{CO} + \text{H}_2\text{O} \rightarrow$ carboxylation,
 V. Cleavage reactions,
 VI. Metathesis, and
 VII. Hydroxylation.
 Especially reaction number I is important for detergents industry.

- | | | | |
|---|--|-------------------|-------------------------|
| Ⓘ | addition of bisulfite or SO_3 | \longrightarrow | sulfo fatty acids |
| Ⓜ | addition of halogen | \longrightarrow | dihalogen fatty acids |
| Ⓝ | addition of HX | \longrightarrow | monohalogen fatty acids |
| Ⓓ | addition of $\text{CO} + \text{H}_2\text{O}$ | \longrightarrow | carboxylation |
| Ⓔ | cleavage reactions | | |
| Ⓟ | metathese | | |
| Ⓡ | hydroxylation | \longrightarrow | hydroxy fatty acids |

Fig. 20. Reactions of double bond

An example for industrial application of cleavage reaction is the cleavage of ricinoleic acid [36, 37]. Metathesis is a reaction in which linear olefins are changed into equimolar active and selective catalysts were developed for metathesis of unsaturated hydrocarbons in homogenous mixtures. They base to WCl_6 and MoCl_5 with $\text{Sn}(\text{CH}_3)_4$, $\text{Sn}(\text{C}_6\text{H}_5)_4$ and $\text{Pb}(\text{C}_6\text{H}_5)_4$ as co-catalysts. These co-catalysts systems enable also meta-

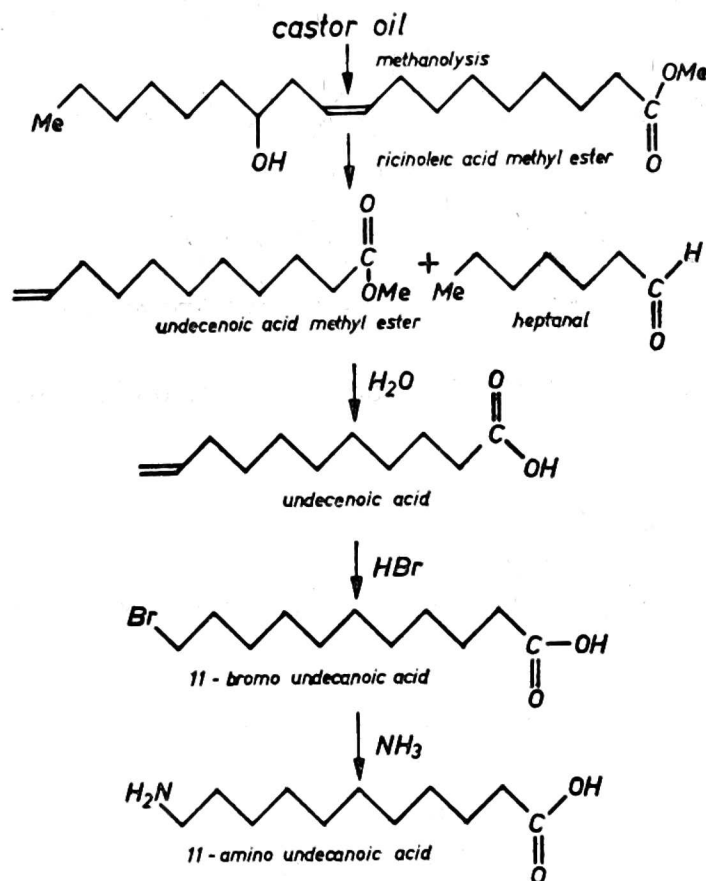


Fig. 21. Synthesis of 11-amino-undecanoic acid

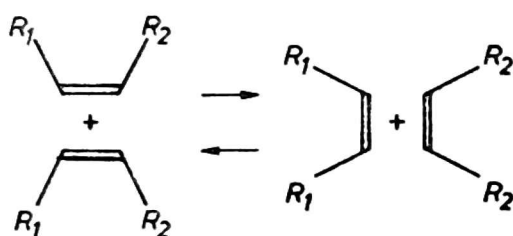


Fig. 22. Metathesis

thesis of the compounds with functional groups like fatty acid esters, halogenated hydrocarbons and so on. Metathesis of fatty acid esters opened a new way to synthesize many compounds which were so far unknown or very difficult to obtain. By hydroxylation of unsaturated fatty acids are yielded hydroxy acids which are used as feed materials for surfactants.

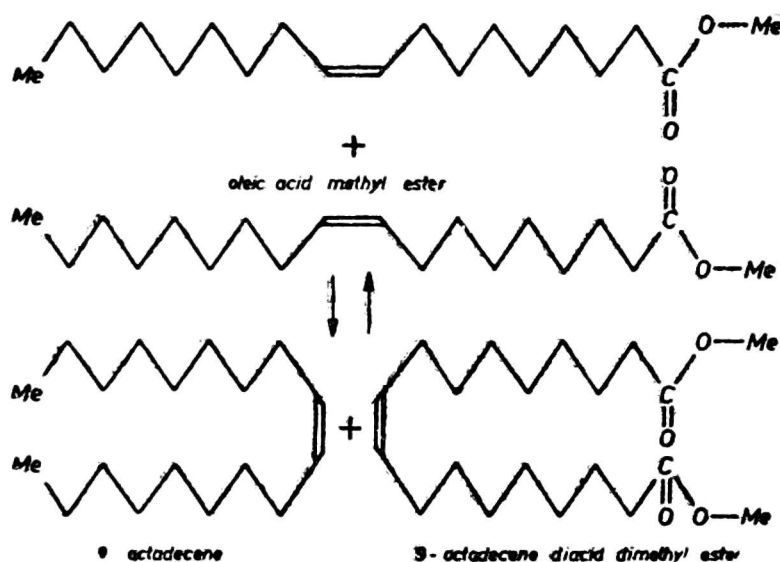


Fig. 23. Synthesis of metathesis products from oleic acid methyl ester

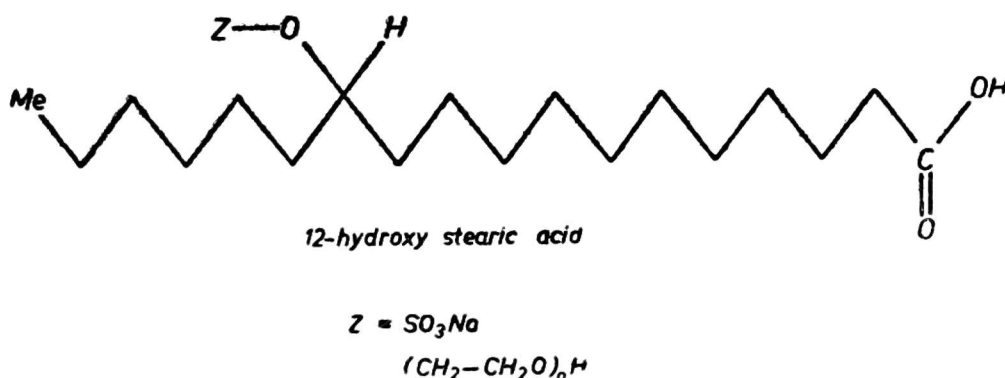


Fig. 24. Reactions of the hydroxylic group

REACTIONS OF THE HYDROXYLIC GROUP

Both reactions are very important for the production of detergents. The principles of reactions with hydroxy fatty acids on hydroxy group and with alcohols are the same.

COMPETITIVE REACTIONS ON SEVERAL REACTIVE CENTRES

The following are the reactions on the carboxyl group:

- I. Preparation of ethyl esters, and
- II. Preparation of N-alkyl- and N,N-dialkyl amides.

The following are the reactions of the double bond:

- I. Preparation of 12-hydroxy stearic acid esters and amides through hydrogenation of their corresponding ricinoleic acid derivatives.
- II. Preparation of undecen-(10)-acid derivatives. By sulfation on OH-group and neutralization, we get two series of compounds [39].

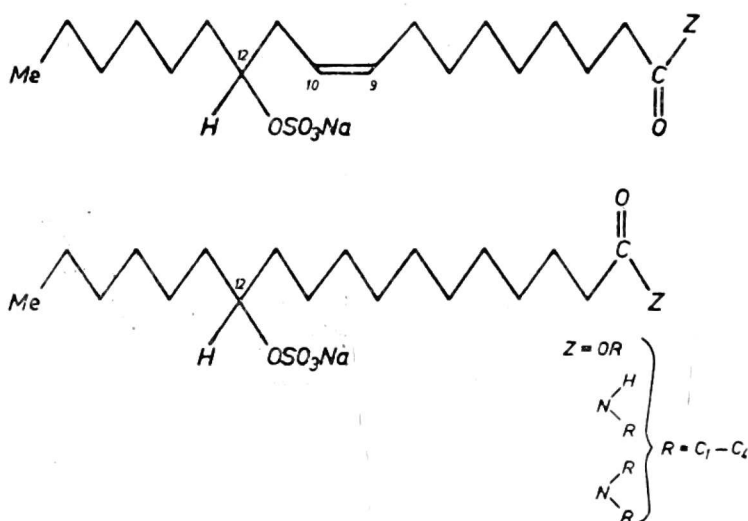


Fig. 25. Reactions of ricinoleic acid and 12-hydroxy stearic acid

We would like to inform you about the measurements of σ/lgc -isotherms, of wetting power, detergency and contact angle in water solutions of the both compounds series. These show characteristic changes in interfacial activity with variation of alkyl radicals R in the structures of homologous series.

Surface tension depends on the substitutions with nitrogen atom. Decreasing of surface tension is considerable with increasing alkyl chain and critical micelle concentration (CMC) is shifted to lower concentrations. The derivative of diisobutylamide show the highest decrease in the surface tension but in case of di-*n*-butylamides it is distinguished very little (curves 3 and 4). Sodium dodecyl sulfate show the almost same decrease of surface tension. However the CMC point of σ/lgc -isotherm is shifted still to lower concentrations about one tenth power (curve 5).

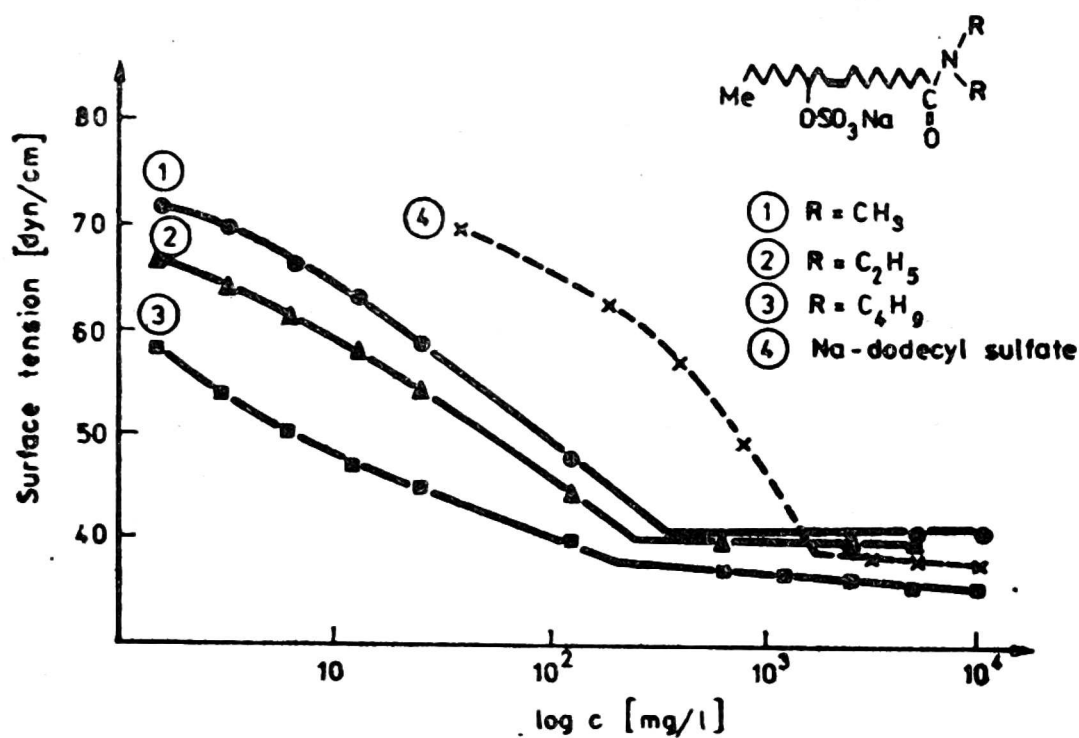


Fig. 26. Surface tension isotherms of ricinoleic acid derivatives

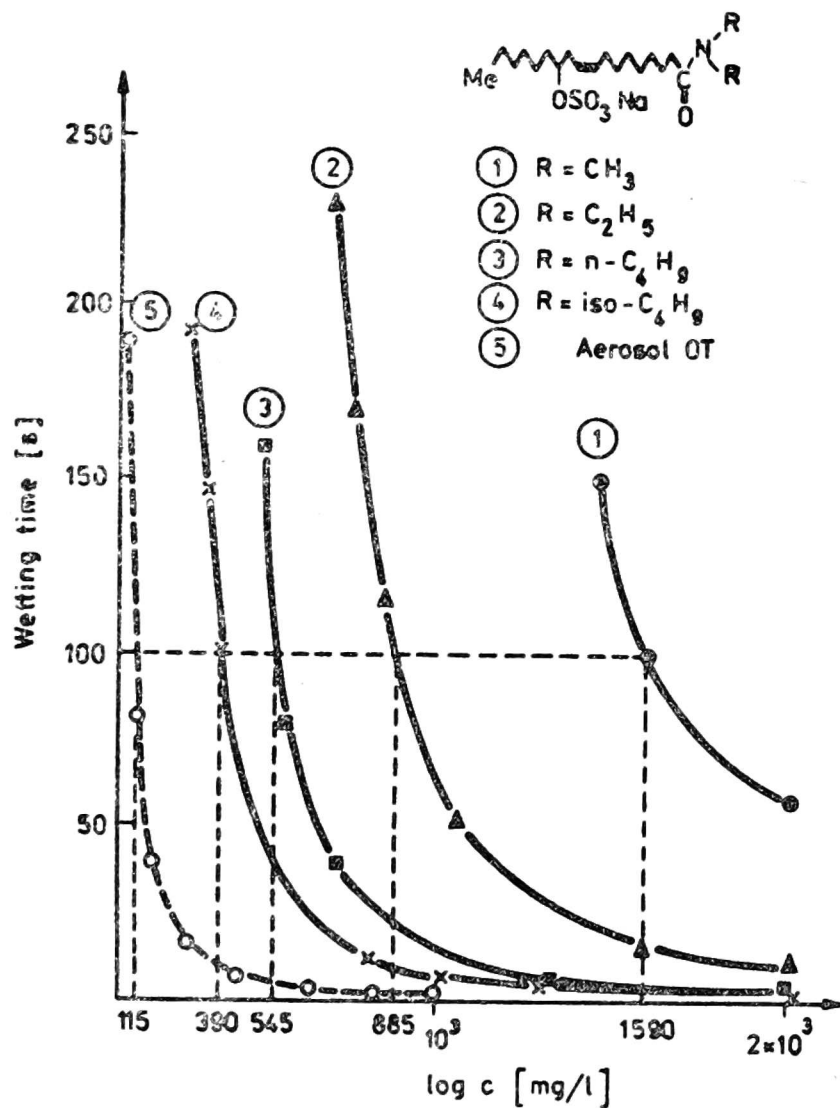


Fig. 27. Wetting power of ricinoleic acid derivatives

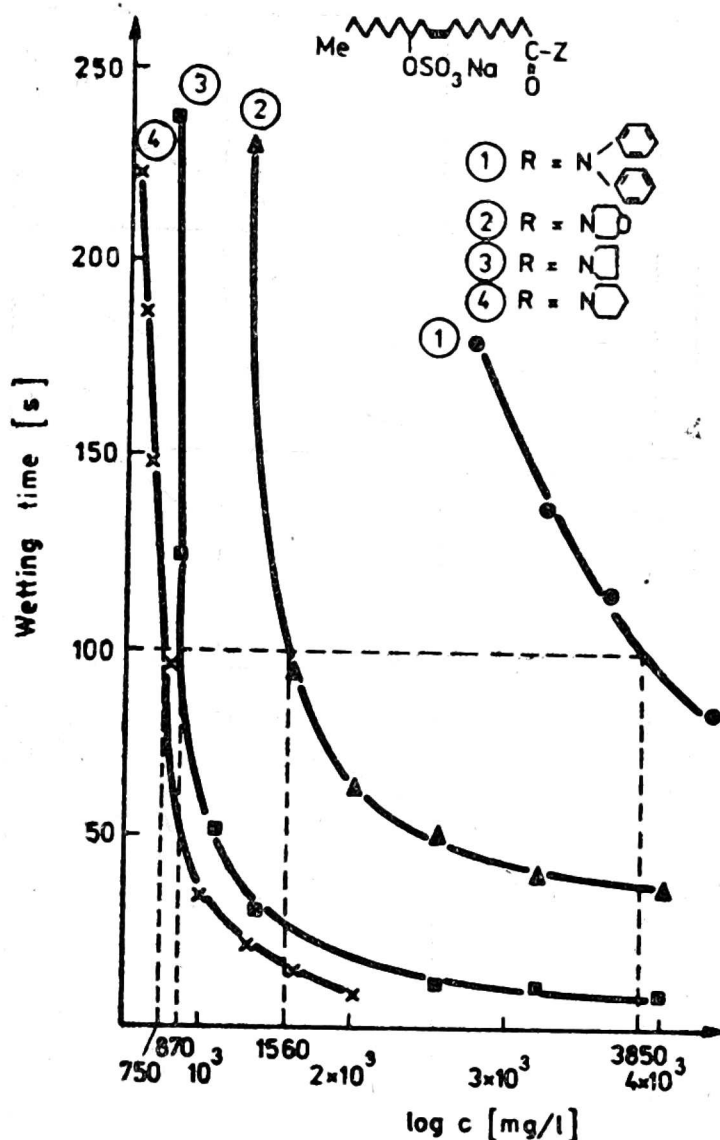


Fig. 28. Wetting power of ricinoleic acid derivatives

With longer alkyl chain on nitrogen, the concentration reached to the value of 100" is smaller, it means that wetting power has been improved. Di-isobutyl compound is in range of very good wetting agents like aerosol OT (curves 4 and 5).

Here, interesting points is that phenyl amide derivate is not possible to the tested according above mentioned methods because of its unfavorable wetting power. But since the benzyl derivative has one more CH_2 group it gives a measurable 100"-value (curve 2).

The compounds of pyrrolidide as well as piperidide have the similar properties. When the ring is extended by one carbon, the value of the compounds becomes better (curves 4 and 5).

On comparison of relation between individual homologous series, it shows dependency characteristically on structure (saturated and unsaturated acid alkyl ester and N,N-dialkyl amide derivatives) [40].

The anionics are soluble in water and also in organic solvents (ethanol, acetone, acetic acid ethyl ester, carbon tetrachloride) while the ester

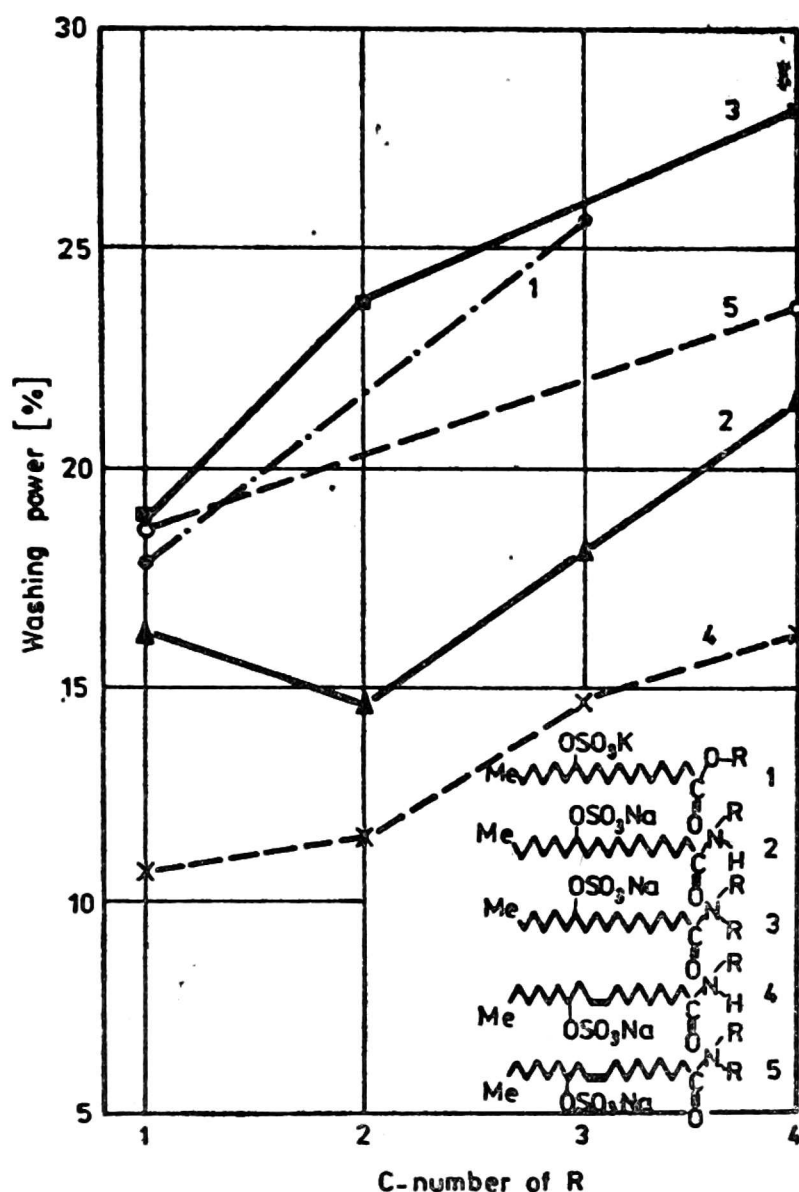


Fig. 29. Washing power of 0.1% — solutions of 12-hydroxy-stearic acid and ricinoleic acid derivatives

sulfates are better soluble than amide sulfates. Ester sulfates are even soluble in diethyl ether. Unsaturated derivatives are better soluble in organic solvents. The gradual increased quantities of the critical micelle concentrations (CMC) are similar for different homologous series, however, CMC values are in different concentration ranges.

The investigations of washing power with jerky laboratory washing machine (EMPA cotton cloth) show characteristic dependency on all homologous series.

The washing power is increased with increase of alkyl chain R .

The saturated compounds possess better detergency than unsaturated compounds. The derivatives of mono (curves 2 and 4) as well as dialkyl amide (curves 3 and 5) which are di-substituted amide sulfates show better detergency than mono-substituted compounds. Our measurements show that there is a correlation between wetting power and

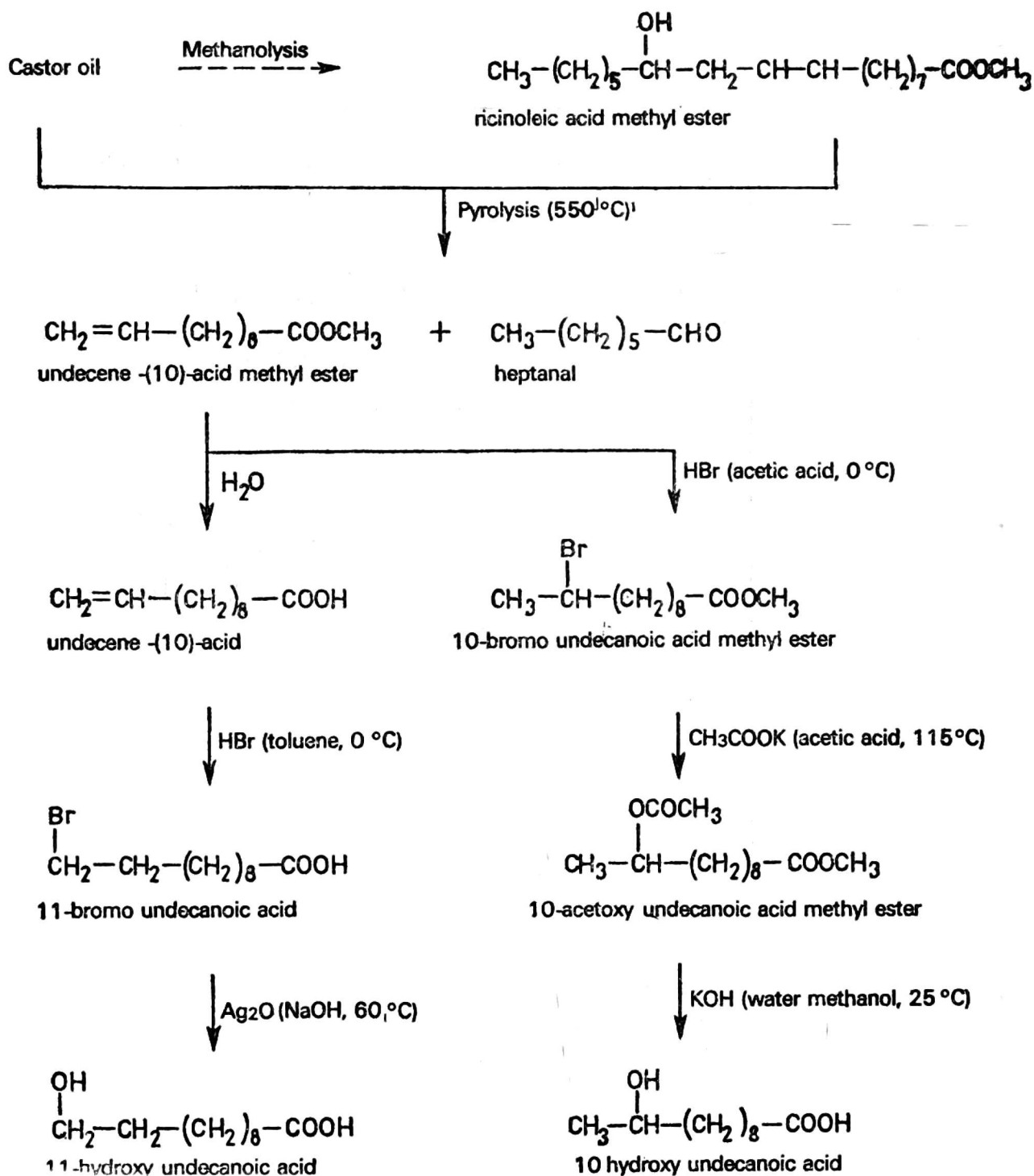


Fig. 30. Synthesis of 10- and 11-hydroxy undecanoic acid

detergency. The compounds with better wetting power also possess better detergency. As detergency is increased CMC-value is decreased since CMC-value is decreased as hydrocarbon chain becomes longer.

We summarize the following regarding to the influence of structure on the investigated compounds:

I. Within a homologous series of ester or amide derivatives, there is a characteristic change in surface active properties by variation of alkyl R.

II. Ester sulfates are hydrolyzed easier than amide sulfates but ester sulfates have better detergent properties in water solution.

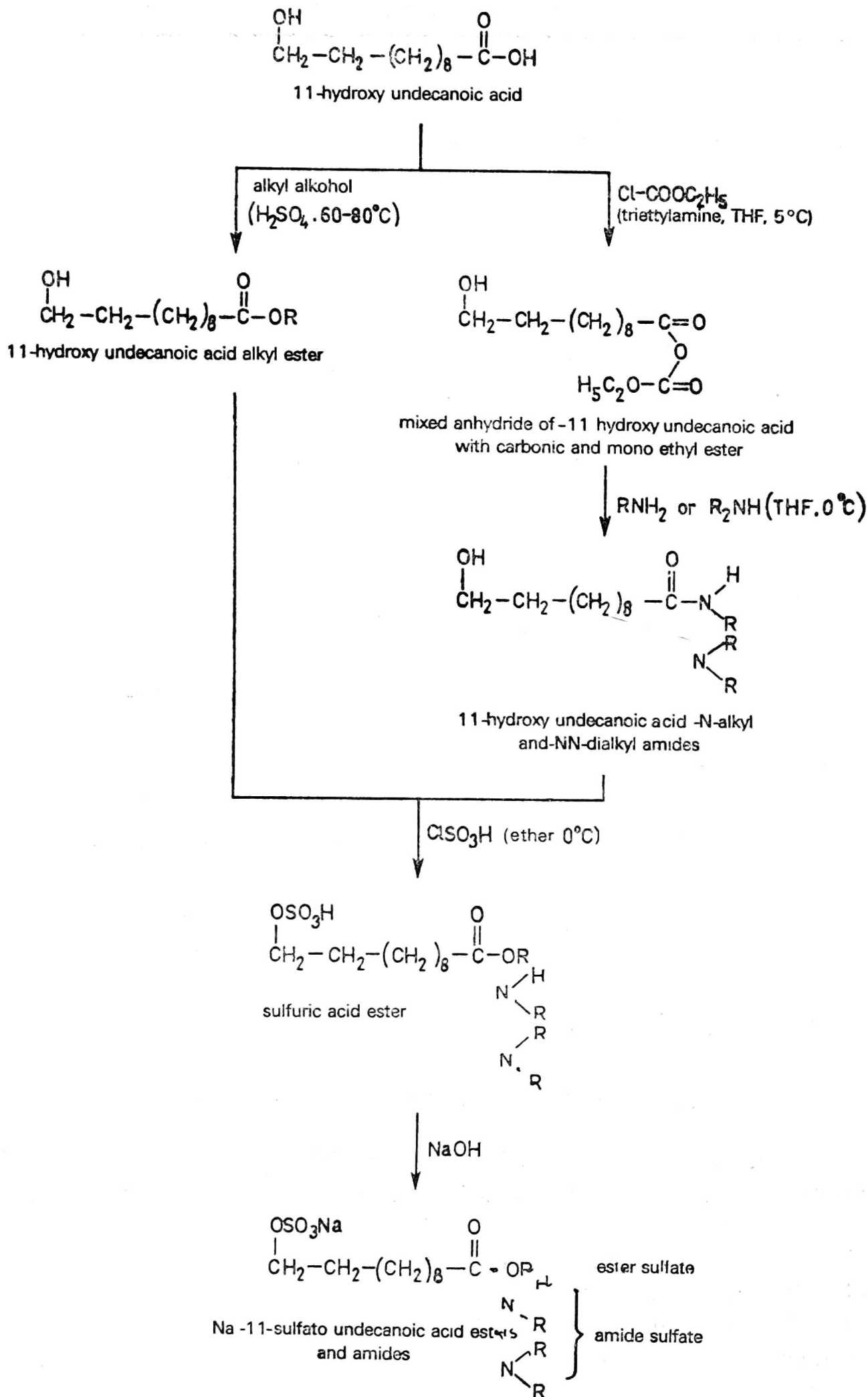


Fig. 31. Synthesis of Na-11-sulfatoundecanoic acid esters and amides from 11-hydroxy undecanoic acid

III. Saturated compounds have better properties than unsaturated compounds of the same constitution.

Some anion active Tensides from undecene-(10)-acid [41]: Undecene-(10)-acid methyl ester (undecylene acid methylester) and heptanal are obtained by thermal cleavage of ricinoleic acid methyl ester.

Undecene-(10)-acid is transferred into 11-amino undecanoic acid via 11-bromoundecanoic acid on industrial scale. This is used for the production of polyamides 11 "Rilsan" [36, 37].

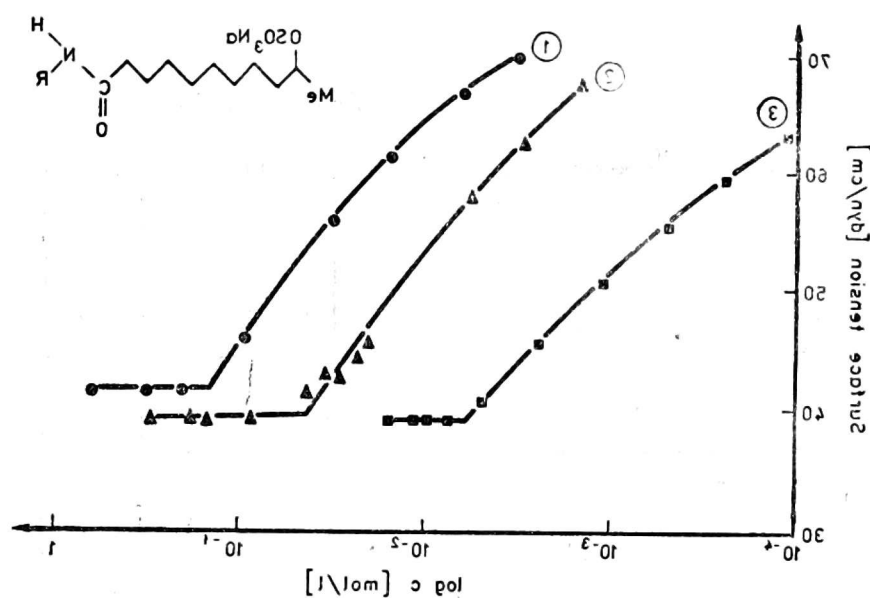


Fig. 32. Surface tension isotherms of undecanoic acid derivatives

We have synthesized 10- and 11-hydroxyundecanoic acid from undecene-(10)-acid via bromoacids. Both acids were transferred into alkylester, N-alkyl and N,N-dialkylamides. Anion active detergents are obtained by sulfation of these compounds on hydroxy group and afterwards

	CMC [mol/l]	σ_{CMC} [dyn/cm]
	$1,5 \cdot 10^{-2}$	40,5
	$9,2 \cdot 10^{-2}$	51,9
	$2,3 \cdot 10^{-2}$	38,8
	$1,5 \cdot 10^{-1}$	41,5

Fig. 33. CMC and σ_{CMC} -values of ester- and amid sulfates

neutralization. Surface active properties of the compounds were investigated and compared.

The substances soluble in water but also in methanol and ethanol are obtained.

Also here we can observe the characteristic decrease of CMC-value with increase of alkyl radical.

On changing over from ester to amide sulfate, the CMC-value is shifted by tenth power on increase of concentration (10- as well as 11-derivatives).

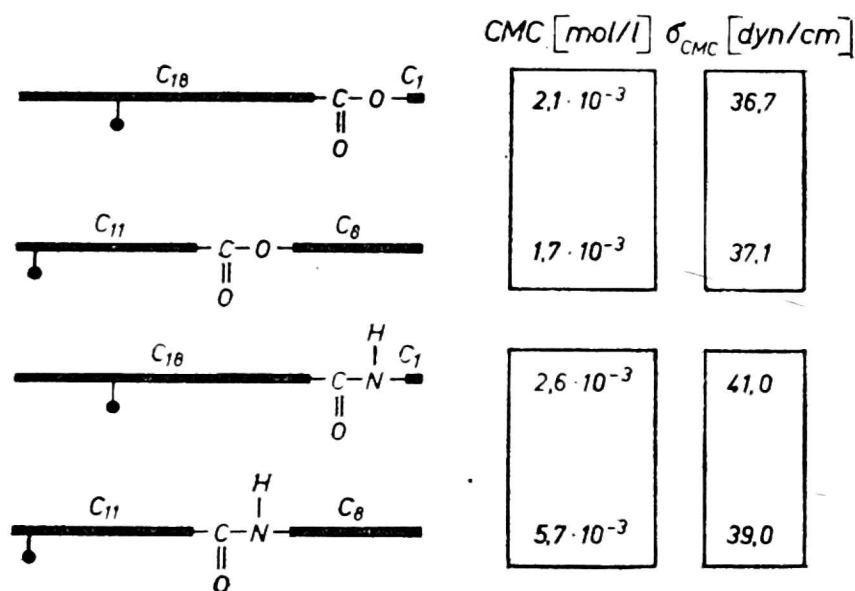


Fig. 34. CMC and σ_{CMC} of similar structure octadecanoic acid and undecanoic acid derivatives of identical molecular weight

In water solutions, ester sulfate reduces the surface tension more than amide sulfate. The surface tension on CMC-point is influenced by the position of sulfate group. CMC-values of the derivatives with secondary sulfate group are lower than corresponding derivatives with primary sulfate group.

Interesting is the comparison between octadecanoic acid and undecanoic acid derivatives having the same olecular weight and similar structure.

Here comparison between two pairs of anion active agents with internal sulfate groups is being shown (ester sulfate, amide sulfate).

In each case one of the both compounds is a derivative of 12-hydroxy octadecanoic acid and other of 10-hydroxy undecanoic acid having similar structure (carbon atom of carboxylic group counted ich each case to alkyl chain C_{18} and C_{11}).

In one pair, both compounds have the same molecular weight but different positions of amid and ester group in hydrocarbon chain. It shows

that there is no effects on interfacial activity if ester function is changed in the chain. Also CMC- as well as σ_{CMC} -value are almost the same.

Also by analogous shift of amid function the Tenside activity is influenced just little. Also there is small difference in wetting power.

Many types of Tensides and other chemicals can be synthesized by proper selection of raw materials from fats and oils.

A simple method for forming a Tenside molecule is that one hydrophobic group and other hydrophilic group are combined together.

Hydrophobic chain, nature of the hydrophilic group and its position in molecule have significant effects on the interfacial activity of the investigated Tenside.

As we have already seen that many surface active agents have not so simple construction. One molecule can have two hydrophilic or two hydrophobic groups and often there is an intermediate group between these two groups. It is also not easy in each case to distinguish that which part is hydrophilic or hydrophobic. So structure and interfacial properties should be taken into account of the Tenside before their application.

Technical and commercial developments of the soap, surfactant and detergent industries leads to the growth of production of fatty acid derivatives. In future such Tensides as soaps and oxyethylated fatty alcohols will be of more importance [42, 43]. Both types are of prominent biological degradation. Oxyethylated primary and secondary alcohols have great washing power against synthetic fibres. One aspect with introduction of phosphate-free washing agents an increase of production of these nonionic Tenside which are insensitive against water hardness.

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NIEKTÓRE POCHODNE DŁUGOŁAŃCUCHOWYCH ALIFATYCZNYCH KWASÓW TŁUSZCZOWYCH

Streszczenie

Długołańcuchowe alifatyczne kwasy karboksylowe są głównym składnikiem tłuszczów oraz olejów roślinnych i zwierzęcych. Te kwasy tłuszczowe są ważne z punktu widzenia odżywczego, medycznego i technologii przemysłowej. Chemią kwasów tłuszczowych zajmowano się już od przeszło 150 lat. Zostało opublikowanych wiele prac naukowych i technicznych. Przedstawiona praca dotyczy niektórych specyficznych aspektów chemii długołańcuchowych kwasów i ich zastosowania w technologii przemysłowej. Przedyskutowano reakcje chemiczne następujących centrów aktywnych w cząsteczce kwasu tłuszczowego:

— reakcje wymiany wodoru, szczególnie w położeniu α w stosunku do grupy karboksylowej,

— reakcje podwójnego wiązania, grupy hydroksylowej lub grupy karboksylowej,

— konkurencyjność reakcji tych centrów reaktywnych.

Szczegółowe rozważania prowadzą do określenia:

1) procesów stosowanych w przemyśle do produkcji środków powierzchniowo czynnych (detergentów, środków zwilżających, emulgatorów),

2) zależności własności od modyfikacji chemicznej struktury cząsteczki.

Г. Рейнheckель, Г. Чихоцки

НЕКОТОРЫЕ ПРОИЗВОДНЫЕ ДЛИННОЦЕПНЫХ АЛИФАТИЧЕСКИХ ЖИРНЫХ КИСЛОТ

Резюме

Длинноцепные алифатические карбоксильные кислоты являются составным элементом растельных и животных жиров и масел. Эти жирные кислоты важны с точки зрения питательной, медицинской и промышленной технологии. Химией жирных кислот занимаются уже свыше 150 лет. Опубликован ряд научных и технических трудов по этому вопросу. Настоящий труд касается некоторых специфических аспектов химии длинноцепных кислот и их использования в промышленной технологии. Обсуждаются химические реакции следующих активных центров в молекуле жирной кислоты:

— реакции обмена водорода, особенно в положении α по отношению к карбоксильной группе,

— реакции двойной связи, гидроксильной или карбоксильной группы,

— конкуренционность реакций этих реактивных центров.

Подробные обсуждения приводят к определению:

1) процессов используемых в промышленности для производства поверхностно-активных средств (детергентов, смачивающих веществ, эмульгаторов),

2) зависимости свойств от химической модификации структуры молекулы.