SUCROSE ESTERS AS SURFACTANTS FROM RENEWABLE RESOURCES

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DEDICATED

TO THE MEMORY OF

MY FATHER

CERTIFICATE

CERTIFIED that the work incorporated in the thesis entitled "Sucrose Esters as Surfactants from Renewable Resources", submitted by Shri KAULGUD RAJEEV ANANT was carried out by the candidate under my supervision. Such material as has been obtained from the other sources, has been duly acknowledged in the thesis.

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CHAPTER—I

INTRODUCTION

I. (a) GENERAL INTRODUCTION

Sucrose [57-50-1], popularly called sugar is produced in far larger quantities in the world as compared to any other organic chemical. World sugar production was 106×10^6 metric tonnes, in 1989-90[1] as compared to 57.4×10^6 tonnes for ethylene[2], the next one in the list. Despite this abundant availability only about 0.1 wt% of sugar is consumed as chemical feedstock.[3] The potential value of sugar as a raw material for the chemical industry was recognized long ago and considerable research has been carried out towards this end.

This interest in sucrose as a raw material has given rise to the entire new branch of carbohydrate chemistry, named as Sucrochemistry. Number of diverse uses for sucrose and its compounds have been proposed and patented[4], though in practice very few applications have been successfully developed. Being an agricultural product, it has certain edge over non-renewable feedstocks such as petroleum-based products; and of late it may also become cost competitive with rising crude prices. Its use for the production of alcohol which is used as petrol substitute in Brazil[5] is one such example.

The other possible use of sugar can be as a raw material for surfactants. Sucrose esters prepared from sucrose and long chain fatty acids preferably C_{14}-C_{18} were reported to be very good

surfactants[6-9] and two broad outlets were considered, important one of them being as household detergents. As these sucrose esters hydrolyze in stomach to form the normal food components, sugar and fatty acids, these non-ionic surfactants can be expected to be both non-toxic and nutritional and can be used as surfactants and emulsifiers in food industry such as instant and frozen foods, confectionery coatings, flavour concentrates and also in cosmetics and pharmaceuticals.

The most important factor in the use of sucrose esters as detergents is their total biodegradability. On the other hand, the linear alkylbenzenesulfonate the current favourite ingredient in household detergents is not totally biodegradable under anaerobic conditions.[10] Sucrose esters are also non-allergic, non-toxic and non-irritating to skin.

Our country is largest sugar producer in the world producing about 10% of world's sugar output of 106×10^6 tonnes and also we have abundant supply of non-edible oilseeds.[11] Estimated potential availability of tree borne oilseeds, which are traditionally not used for extracting edible oils is about 7.6×10^6 tonnes per annum.[11] These comprise mostly of Sal, Mohwa, Neem, Karanja, Kokum, Pilu, Rubber seed etc. The oils obtained from these seeds can be a very good source of acidic segment of sucrose esters.

This study was undertaken with following three important aspects :

1. Sucrose esters are very good detergents comparable to sodium dodecylbenzenesulfonate, the main active ingredient of almost all the popular detergents in the market. Sucrose esters are non-toxic and totally biodegradable compounds and as such do not create any pollution problem.

2. Both the raw materials required are indigenously available from renewable resources as they are derived respectively from cane-sugar and abundantly available oilseeds in our forests, which are being used in very limited quantities at present. The collection of these oilseeds is mainly carried out by Adivasis and other tribal people. The seed collection activity would help them getting some badly needed financial assistance, thus serving a major social purpose.

3. Increasing use of sugar esters would reduce the strain on our foreign exchange as the current detergent ingredients depend heavily on imported petroleum products as raw materials.

The preparation of sucrose esters can be achieved by transesterification process, involving migration of acidic segment from original ester to the new alcohol forming new ester and regenerating parent alcohol of the original ester. Thus,

$$RCOOR' + R''OH \xrightarrow[(OH)^-]{H^{(+)}} RCOOR'' + R'OH$$
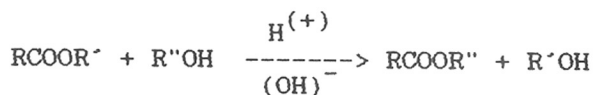
Where, R, R' and R'' are alkyl groups.

The naturally available oils are essentially the triglycerides of the general formula (I).

$$
\begin{array}{l}
CH_2.O.COR \\
CH.O.COR´ \\
CH_2.O.COR''
\end{array}
$$
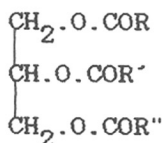
(I)

Where R, R´ and R" are straight chain saturated, mono/poly unsaturated alkyl groups containing mostly $C_{12}-C_{20}$ straight chains. The exact composition varies in various oils.

TABLE-I gives fatty acid composition of eight oils used in this study. These include 4 tree borne non-edible oils[11] viz. Sal, Mohwa, Neem, Pilu; 2 other abundantly available non-edible oils i.e. Castor and Rice Bran oil[11]; and two edible oils viz. Groundnut[12] and Coconut oil[11]. These two edible oils were considered as useful towards preparation of sucrose esters which would be useful in food and pharmaceutical industry. TABLE-II lists various properties of fats obtained from these oilseeds and their oil contents.

In the following paragraphs the chemistry and applications of sucrose and these tree borne oils and other oils is covered briefly.

TABLE-I

Sr.No.	Name of the acid	Sal Oil	Mohwa Oil	Pilu Oil	Castor Oil	Rice Bran Oil	Groundnut Oil	Coconut Oil
1.	Caproic acid	-	-	-	-	-	-	0.2 - 0.5%
2.	Caprylic acid	-	-	-	-	-	-	5.4 - 9.5%
3.	Capric acid	-	-	1.0 - 1.5%	-	-	Traces	4.5 - 9.7%
4.	Lauric acid	-	-	19.6-47.2%	-	-	Traces	44.1-51.3%
5.	Myristic acid	-	-	28.4-54.5%	-	0.4 - 0.6%	-	13.1-18.5%
6.	Palmitic acid	4.5 - 8.6%	16.0-28.2%	18.9-19.5%	-	11.7-16.5%	8.3%	7.5 -10.5%
7.	Stearic acid	34.2-44.2%	20.0-25.1%	-	-	1.7 - 2.5%	3.1%	1.0 - 3.3%
8.	Arachidic acid	6.3 -12.2%	0.0 - 3.3%	-	-	0.4 - 0.6%	2.4%	0.0 - 1.5%
9.	Behenic acid	-	-	-	-	-	3.1%	-
10.	Lignoceric acid	-	-	-	-	0.4 - 0.9%	1.1%	-
11.	Oleic acid	41.4-42.2%	41.0-51.0%	5.5-12.0%	-	39.2-43.7%	56.0%	5.0 - 8.2%
12.	Linoleic acid	2.7%	8.9 -13.7%	0.0 - 1.3%	4.5 - 5.0%	26.4-35.1%	26.0%	1.0 - 2.6%
13.	Linolenic acid	-	-	-	-	-	-	-
14.	Ricinoleic acid	-	-	-	91.4-94.9%	-	-	-

TABLE-II

Sr.No.		Sal Oil	Mohwa Oil	Pilu Oil	Castor Oil	Groundnut Oil	Coconut Oil	Rice Bran Oil
A	Oil content in seeds	14-20%	46-53%	40-43%	45-49%	48.4%	63-70%	15%
B	Properties of fat							
1.	Colour	Yellowish green	Pale Yellow	Green	Pale Yellow	Greenish Yellow or almost colorless	White or almost colorless	Golden Yellow
2.	Consistency	Hard & brittle	Plastic	-	Thick, viscous oily (wax like) liquid.	-	Soft, Smooth semi-solid or liquid	-
3.	Melting or congealing point	35.2°C (m.p.)	25-29°C (m.p.)	41°C (m.p.)	-10°C to -18°C (c.p.)	-5°C (c.p.)	24-25°C (m.p.)	-
4.	Specific gravity (at 30°C)	0.8692	0.856-0.870 (at 15°C)	0.867	0.958-0.968 (at 15°C)	0.910-0.921 (at 20°C)	0.9150	0.901-0.9059 (at 25°C)
5.	Refractive index (at 40°C)	1.4579	1.452-1.462	1.450	1.466-1.473	1.4605-1.4645	1.4477-1.4495	1.470-1.474
6.	Saponification value	190.0	187-196	231-247	177-187	188-195	251-263	117-199
7.	Iodine value	37.9	58.0-70.0	5.5-7.6	82-90	84-102	8.0-9.6	84.3-105.3
8.	Acid value	10.6	5-50	-	Max.2	0.08-6.0	Not over 6	4-120
9.	Unsaponifiable matter	0.91%	1.0-3.0%	0.9%	0.3-0.7%	0.8%	Nil	3.0-5.0%

I.   b) **THE CHEMISTRY OF SUCROSE**

Sucrose   is   a   non-reducing   disaccharide   which   is
systematically named β-D-fructofuranosyl α-D-glucopyranoside.   In
this molecule, the hexose sugars D-glucose [50-99-7] and D-
fructose [57-48-7] are combined through their glycosidic hydroxyl
groups.

Glucose   is in the α-pyranose ring form and fructose   is   in
the β-furanose ring form.   The numbering of the carbon position
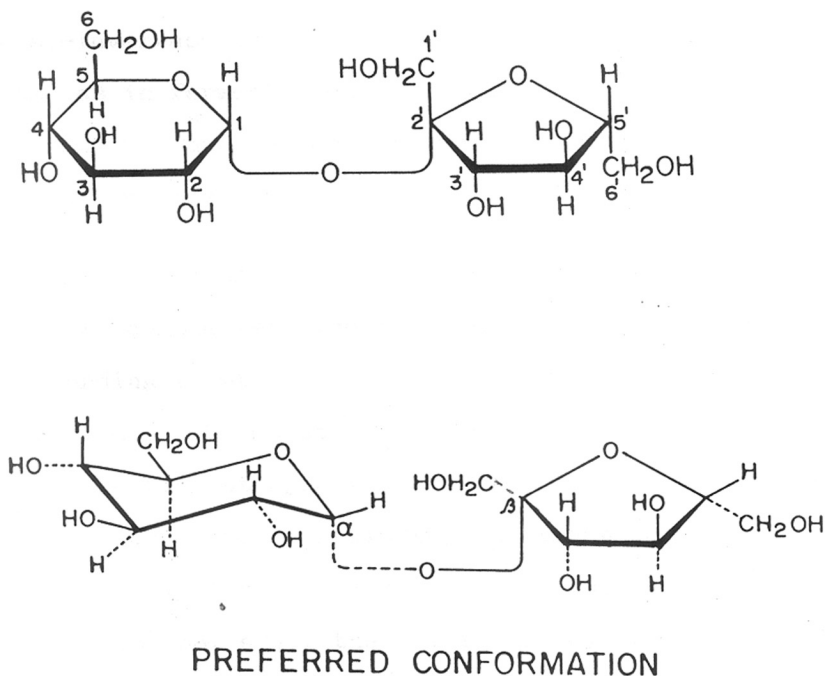or the hydroxyl groups is shown in Figure 1.

PREFERRED CONFORMATION

FIGURE-1: SUCROSE $(C_{12}H_{22}O_{11})$

Sucrose contains eight hydroxyl groups three of which are primary (C-6, C-6´, C-1´) and the remaining five are secondary (C-2, C-3, C-4´, C-4, C-3´). The structure of sucrose has been established both by chemical[13-16] and enzymic syntheses[17-19]. Its structure was further confirmed by physical methods such as X-ray crystallography,[20,21] neutron diffraction[22] and nuclear magnetic resonance spectroscopy.[23,24]

Sucrose is relatively stable, since it lacks the potential free carbonyl group of a reducing sugar and has the chemical properties of an octahydric alcohol. It is, however, readily hydrolyzed to its component hexoses by the appropriate enzyme, e.g. yeast-invertase or by acid catalysis. Thus, in degradative reactions as in fermentation (qv), sucrose generally loses its unique identity and gives similar products as a mixture of glucose and fructose under equivalent conditions.

The synthetic chemistry of sucrose is that of a polyhydric alcohol in which the relative reactivities of the hydroxyl groups differ according to whether they are primary or secondary and to their position in the molecule. This leads to the possibility of selective reaction at specific position on the sucrose molecule and multiple substitution including an almost infinite diversity of potential derivatives. Differences in reactivity depends on a number of factors, e.g., the solvent used, type of reaction, steric interference and temperature. Generally, the primary

hydroxyl groups are the most reactive than the secondary hydroxyl groups occupying the positions 2-, 3-, 3´-, 4- and 4´- of the sucrose molecule.

Sucrose is insoluble in most organic solvents, so that reactions in solutions require the use of polar or hydrogen bonding solvents.[25] Solubility of sucrose in gms per 100 gms of solvents at 100°C is listed below.

Pyridine	5.9 gms
Dimethyl Sulfoxide	58.7 gms
N,N-dimethylformamide	29.6 gms
Hexamethylphosphoric triamide.	Very soluble

Among these, dimethyl sulfoxide and N,N-dimethylformamide are used frequently. Sometimes, the reactions are carried out in the aqueous medium and very rarely in the absence of solvents. The need for using costly polar solvents (which are difficult to recover) is frequently a determining factor in the economics of commercial derivatives prepared from sucrose.

Sugar, primarily sucrose can be viewed as a chemical raw material in addition to its use as a food product. The great advantage of sucrose as a raw material is that the supplies are renewable annually, unlike depleting supplies of raw materials such as petroleum and coal. Currently, sugar is used as a raw material in the production of Citric acid and Sorbitol.

I   c) (i) SYNTHETIC DERIVATIVES

Sucrose undergoes those reactions characteristic of alcohols giving, for example, esters, ethers, acetals and urethanes. The hydroxyl groups can be replaced by hydrogen, halide, azide, amino, thiol, nitrile, thiocyanate, thioacetate and other monovalent groups. The primary hydroxyl groups can be oxidised to aldehyde or carboxylic acid and secondary hydroxyl groups to ketone. Unsaturation can be introduced and internal anhydro rings can also be created. The importance of these derivatives as synthetic intermediates has been limited because of the necessity of costly solvents for the reactions and the low yields of the pure derivative. Applications have been developed only for certain esters and ethers in the specialised fields.

(ii)   PREPARATION OF SUCROSE ESTERS

An important route for the preparation of sucrose esters is by transesterification between sucrose and an ester, whereby an acyl group is transferred to sucrose in the presence of a basic catalyst, e.g. Potassium carbonate. The reaction is normally reversible, though the position of equilibrium can be shifted in either direction by continuously removing one component of the reaction, e.g., sucrose heated in solution in dimethylformamide with the methyl ester of a fatty acid in the presence of anhydrous potassium carbonate as a catalyst forms predominantly

the sucrose monoester (mainly the 6 and 6´-isomers) with the liberation of methanol. In the presence of an excess of methyl ester, further hydroxyl groups react to give the di- and higher esters of sucrose. If a triglyceride rather than methyl ester is used, then equilibrium is reached between sucrose and mono and diesters of sucrose and glycerol. If the glycerol is not removed, the reaction remains at its equilibrium composition. Since glycerol mono- and di- esters of fatty acids are effective emulsifying agents and are particularly suited for food applications, the mixture of sucrose and glycerol esters resulting from the reaction of sucrose with natural triglycerides, e.g. tallow, palm oil or coconut oil can be used without further separation.[26] The solvent customarily used in this reaction i.e. dimethylformamide is a costly component both for recovery and elimination from the food grade product. A solventless process has been developed in which sucrose and a triglyceride react in the presence of potassium carbonate as a catalyst at 125°C to give the mixture of sucrose monoesters and glycerol esters directly.[27] The mixed product, known as sucroglyceride can be separated into its component sucrose esters and mono- and di- glycerides by means of food grade solvents.[28]

I.   d) THE CHEMISTRY OF OILS AND FATS

As mentioned earlier oils which are triglycerides are rich source of saturated and unsaturated straight chain fatty acids

containing usually C_8-C_{24} atoms, as these acids are obtained by hydrolysis of oils, which are alternatively known as fats, they are called fatty acids. Glycerol is an important and valuable by-product of this hydrolysis. (Please refer to CHART-1 for structure and names of these acids).

I.   e) **THE APPLICATIONS OF OILS AND FATS**

Apart from sucrose esters, these fatty acids are extensively used[29] for making variety of compounds as shown in CHART-2.

Some of these compounds like alkanolamides and amine ethoxylates are of great commercial value. CHART-3 indicates some of the important amines used to make these compounds along with the reactions.

These various fatty acid derivatives prepared by either, neutralization, esterification, amidation, ethoxylation or condensation of fatty acids with other appropriate compounds find wide applications in cosmetics, detergent powders, detergent liquids, fabric softeners, corrosion inhibitors, textile auxiliaries and food stuffs.

The quaternary salts obtained from these acids are used in phase transfer catalysts. These catalysts have become very popular and have been reported[30,31] to facilitate reactions in aqueous systems and with very mild reaction conditions to give excellent yields otherwise considered impossible.
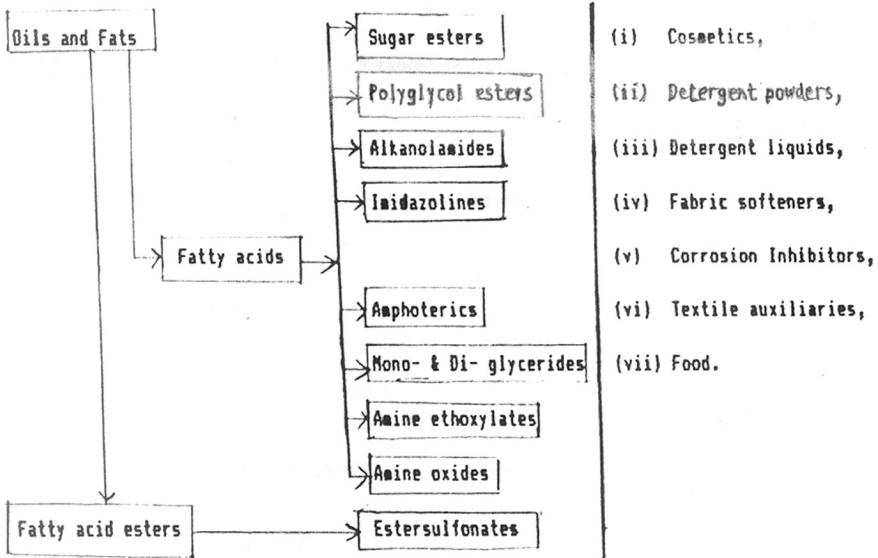
CHART-1

Sr.No.	Generic Name	Structural Formula	Molecular formula	Mol.wt.	Systematic Name
1.	Caproic acid	$CH_3.(CH_2)_4.COOH$	$C_6H_{12}O_2$	116.0	Hexanoic acid
2.	Caprylic acid	$CH_3.(CH_2)_6.COOH$	$C_8H_{16}O_2$	144.0	Octanoic acid
3.	Capric acid	$CH_3.(CH_2)_8.COOH$	$C_{10}H_{20}O_2$	172.0	Decanoic acid
4.	Lauric acid	$CH_3.(CH_2)_{10}.COOH$	$C_{12}H_{24}O_2$	200.0	Dodecanoic acid
5.	Myristic acid	$CH_3.(CH_2)_{12}.COOH$	$C_{14}H_{28}O_2$	228.0	Tetradecanoic acid
6.	Palmitic acid	$CH_3.(CH_2)_{14}.COOH$	$C_{16}H_{32}O_2$	256.0	Hexadecanoic acid
7.	Stearic acid	$CH_3.(CH_2)_{16}.COOH$	$C_{18}H_{36}O_2$	284.0	Octadecanoic acid
8.	Arachidic acid	$CH_3.(CH_2)_{18}.COOH$	$C_{20}H_{40}O_2$	312.0	Eicosanoic acid
9.	Behenic acid	$CH_3.(CH_2)_{20}.COOH$	$C_{22}H_{44}O_2$	340.0	Docosanoic acid
10.	Lignoceric acid	$CH_3.(CH_2)_{22}.COOH$	$C_{24}H_{48}O_2$	368.0	Tetracosanoic acid.

CHART-1 (Contd.)

Sr.No.	Generic Name	Structural Formula	Molecular Formula	Mol.Wt.	Systematic Name
11	Oleic acid		$C_{18}H_{34}O_2$	282.0	cis-9-Octadecenoic acid
12	Linoleic acid		$C_{18}H_{32}O_2$	280.0	cis, cis-9,12-Octadecadienoic acid
13	Linolenic acid		$C_{18}H_{30}O_2$	278.0	cis, cis, cis, -9,12,15-Octadecatrienoic acid
14	Ricinoleic acid		$C_{18}H_{34}O_3$	298.0	cis-9-Octadecenoic acid, 12-hydroxy

CHART-2

Applications of oils and fats

```
┌─────────────┐              ┌─────────────────────┐
│Oils and Fats│          ┌──→│ Sugar esters        │      (i)    Cosmetics,
└─────────────┘          │   └─────────────────────┘
                         │ ┌→│ Polyglycol esters   │      (ii)   Detergent powders,
                         │ │ └─────────────────────┘
                         │ │→│ Alkanolamides       │      (iii)  Detergent liquids,
                         │ │ └─────────────────────┘
                         │ │→│ Imidazolines        │      (iv)   Fabric softeners,
                         │ │ └─────────────────────┘
        ┌────────────┐   │ │
      ..│ Fatty acids│──→│ │                               (v)    Corrosion Inhibitors,
        └────────────┘   │ │ ┌─────────────────────┐
                         │ │→│ Amphoterics         │       (vi)   Textile auxiliaries,
                         │ │ └─────────────────────┘
                         │ │→│ Mono- & Di- glycerides│     (vii)  Food.
                         │ │ └─────────────────────┘
                         │ │→│ Amine ethoxylates   │
                         │ │ └─────────────────────┘
                         │ └→│ Amine oxides        │
                         │   └─────────────────────┘
┌──────────────────┐         ┌─────────────────────┐
│ Fatty acid esters│────────→│ Estersulfonates     │
└──────────────────┘         └─────────────────────┘
```

CHART-3

NH$_2$-CH$_2$-CH$_2$-OH   Monoethanolamine

         CH$_2$-CH$_2$-OH
        /
   NH   Diethanolamine
        \
         CH$_2$-CH$_2$-OH

NH$_2$-CH$_2$-CH$_2$-NH-CH$_2$-CH$_2$-NH$_2$ Diethylenetriamine

NH$_2$-CH$_2$-CH$_2$-NH-CH$_2$-CH$_2$-OH   Hydroethylenediamine

----

Reactions

R-COOH+NH$_2$-CH$_2$-CH$_2$-OH ------> R-CO-NH-CH$_2$-CH$_2$-OH+H$_2$O
                                                     |
                                                     ⋮ R-COOH
                                                     ↓
                          R-CO-NH-CH$_2$-CH$_2$-OCO-R+2H$_2$O

I.   f) SPECIAL APPLICATIONS OF SUCROSE ESTERS

As explained in preceding paragraphs sucrose esters have varied applications and some compounds are being produced commercially in European countries and Japan since 1960. In 1960, the Dai-Nippon Sugar Manufacturing Company, Japan, built a semi-commercial plant to produce about 300 tonnes/year of sucrose esters. In 1967, another plant with a capacity of 1200 tonnes went on stream using the process known as Hass-Snell process involving dimethylformamide as a solvent. In 1967, Osipow and co-workers developed the Nebraska-Snell process in which microemulsion of sucrose is formed in Propylene glycol which is treated with methyl esters of fatty acids. In 1975, Ryoto put in operation a plant to produce 3000 tonnes/annum of sucrose ester. The other major companies which produce sucrose esters are: (a) Rhône-Poulenc of France; (b) Tate and Lyle Ltd., of U.K.

In Japan, sucrose esters are used mostly in food additives and related industries and only about 10% of the product is used as detergents. TABLE-III gives sectorwise applications of sucrose esters.[32] However, it was anticipated that use of sucrose esters as detergent will rise faster in future as compared to food and allied sectors.

Next chapter illustrates the work carried out in this direction for the preparation of sucrose esters mostly from non-edible oils which are available abundantly in our country.

TABLE-III

Current Usage of Sugar Esters in Different Applications

Sr.No.	Application	Percentage use of sugar esters
1.	Cakes and Breads	31%
2.	Emulsified Fat and Oil	
	a) Coffee whitener,	
	b) Whipped cream,	
	c) Recombined milk,	22.3%
	d) Shortening oil,	
	e) Ice cream.	
3.	Instant Food	
	a) Curry,	
	b) Soybean curd,	13.1%
	c) Cocoa,	
	d) Cake-mix.	
4.	Confectionery	
	a) Biscuit,	
	b) Chocolate,	
	c) Chewing-gum,	15.3%
	d) Rice-cake,	
	e) Tablet-candy.	
5.	Detergent	9.3%
6.	others	
	a) Drugs,	
	b) Cosmetics,	9.0%
	c) Chemical Industry.	

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(Symposium Series No.41) pp 85.

CHAPTER—II

PREPARATION OF SUCROSE ESTERS AND DETERMINATION OF THEIR SURFACTANT PROPERTIES

SECTIONS : (A) – PRESENT STUDY

(B) – RESULTS AND DISCUSSIONS

(C) – EXPERIMENTAL

SECTION – A

PRESENT STUDY

PRESENT STUDY

The sucrose esters are known for quite some time and their preparation by various methods have been reported.[1-4] This study was undertaken with a primary view of preparing these esters from non-conventional, non-edible oils obtained from less known seeds from the forests of our country and to ascertain whether they can be used as detergents and/or surfactants like pure compounds as sucrose stearate etc. The oils used possess various combinations of at least ten different fatty acids in the form of triglycerides and it was thought that their separation may not be necessary for use as detergents and hence the detergency properties were compared with sodium dodecylbenzenesulphonate which is a standard and well known compound.

As mentioned earlier, the following oils were used to prepare sucrose esters by four different methods. The experimental details of these four methods are given in the Section C of this chapter.

1) Coconut oil, 2) Groundnut oil, 3) Hydrogenated vegetable oil [Dalda], 4) Sal oil, 5) Rice Bran oil, 6) Pilu oil, 7) Mohwa oil, 8) Castor oil.

A) **Dry Method**[1]

Sucrose, was reacted with various oils in the presence of catalysts such as sodium or potassium carbonate and coconut oil

monoglycerides at an elevated temperature. The reaction mixture which was heterogeneous and very mobile at the beginning of the reaction became homogeneous and viscous as the reaction progressed and started swelling due to evolution of carbon dioxide. Finally, the reaction mixture became very viscous and stirring became very slow and difficult. Apart from these physical changes the reaction was monitored by solubility test. Small samples of the reaction product were withdrawn at fixed time intervals and dissolved in isopropanol or n-butanol. Initially, excess sugar was the only insoluble part in the reaction mixture. As the reaction progressed the percentage of insoluble sugar started dropping down and after a certain stage became almost constant; indicating the end of the reaction. Unreacted Sucrose was removed by successive extraction with isopropanol/n-butanol and the extract after removal of solvent was further treated with petroleum ether to remove unreacted oil leaving behind sucrose esters.

B) Solvent Method[2]

The method consists of reacting methyl or ethyl esters of fatty acids (prepared from various oils), with sucrose in a suitable solvent such as dimethylformamide or dimethyl sulfoxide in the presence of catalysts.

C-1) **Microemulsion technique**

Aqueous System[3]

Methyl esters of oils, sucrose and water (as a reaction medium) were mixed with sodium stearate to form a microemulsion. The reaction was carried out at an elevated temperature and the water was removed under reduced pressure. The total reaction product was extracted with isopropanol/n-butanol to separate a mixture of sodium stearate and sucrose as insolubles. This insoluble part was useful for recycling in the next batch.

C-2) **Microemulsion technique**

Propylene glycol System[4]

This is a similar system as the one described above. The use of propylene glycol instead of water, is the only change in the reaction medium. This facilitates to carry out the reaction at lower temperatures.

The product obtained by all these methods, was essentially a mixture of sucrose monoesters and about ≈5% of di-esters of sucrose. It is well established[5] that the substitution preferentially takes place at the 6th position; while next substitution occurs at the second primary hydroxyl group attached to carbon at the 6′ position of the sucrose molecule (**CHART-2.1**). Monoglycerides, di-glycerides and glycerol in small amounts were

CHART-2·1

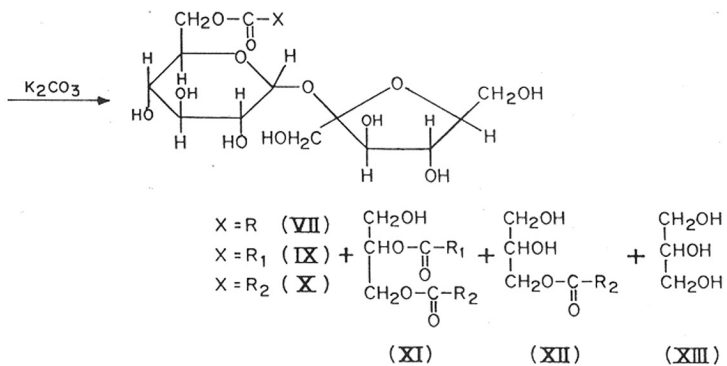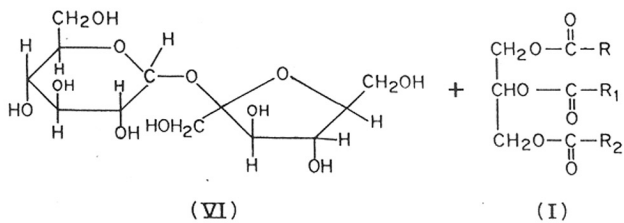### 1) PREPARATION OF METHYL ESTERS:
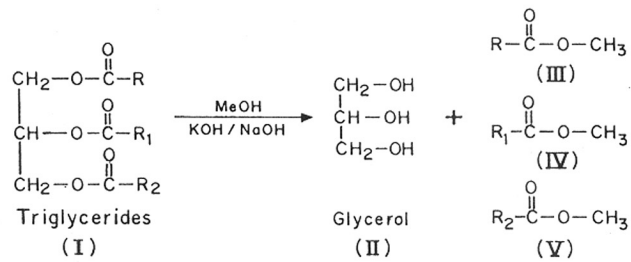
WHERE R, R$_1$ AND R$_2$ ARE STRAIGHT CHAIN SATURATED
OR UNSATURATED ALKYL GROUPS WITH USUALLY
11-17 CARBON ATOMS. IN THE CASE OF RICINOLEIC
ACID THERE IS A HYDROXY SUBSTITUENT ON
THE 12th CARBON ATOM.

2) PREPARATION OF SUCROSE ESTERS BY USING SOLVENT SUCH AS DMF:
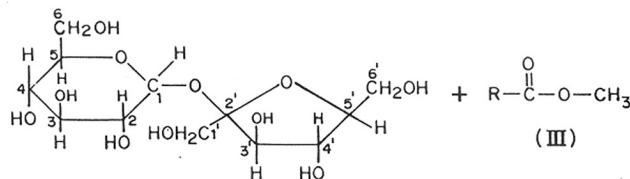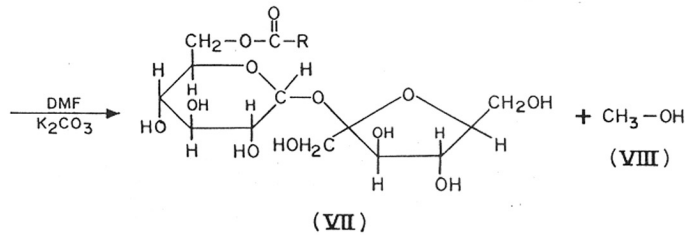
3) DRY METHOD FOR PREPARATION OF SUCROSE ESTERS:

(VI)   (I)

$X = R$ (VII)
$X = R_1$ (IX) +
$X = R_2$ (X)

(XI)   (XII)   (XIII)

obtained as by-products when method (A) was employed. Though it is not mentioned in the equation 3 there can be two more di-glycerides and two more mono- glycerides depending on which particular acidic portion from triglycerides is taking part in transesterification.

As the major objective of the study was to prepare surface active compounds, the purification of the reaction mixture was restricted to obtain sucrose esters. This was achieved by following steps.

1) Removal of solvent by distillation

When the reactions were carried out using solvents such as DMF [Dimethylformamide] or DMSO [Dimethyl sulfoxide] or employing microemulsion technique, the solvent was distilled out after the reaction under reduced pressure.

2) Extraction of reaction product with isopropanol/n-butanol

The reaction product obtained after removal of solvent was extracted with isopropanol/n-butanol to remove unreacted sucrose as insoluble solids. This also facilitated the removal of any polymeric impurities formed during the reaction.

3) Extraction with petroleum ether

The isopropanol/n-butanol extract of the reaction product was filtered and concentrated to dryness. It was then refluxed

with pet.ether and decanted to remove unreacted oil and glycerides which were formed during the course of reaction as pet.ether solubles. The insoluble waxy solid left behind was called as sucrose esters.

4) Removal of last traces of solvent

This was achieved by heating the sucrose esters obtained after pet.ether extraction for about 30 minutes at 75-80°C at 3-5 mm of Hg pressure.

All the reaction products obtained after the above mentioned purification steps are denoted by using suffix "G" in subsequent discussions.

No attempts were made to separate individual sucrose ester such as sucrose laurate, sucrose oleate, etc., from the reaction mixture.

Determination of various surface active properties

The following surface active properties were determined :
1) Detergency, 2) Surface tension, 3) Draves' wetting test, 4) Foam height, 5) Emulsification, 6) Lime soap dispersant requirement.

CMC [critical Micelle concentration] values were derived from surface tension data by plotting the graph of surface tension against logarithm of concentration. Some of the initial results from this study have already been published.[6-7]

SECTION — B

RESULTS AND DISCUSSIONS

RESULTS AND DISCUSSIONS

A) Detergency

The detergency values obtained for various sucrose esters are tabulated in **TABLE 2.1**. Sodium dodecylbenzenesulfonate, an active ingredient of most of the commercial detergents was chosen as a standard compound for reference. The percent detergent efficiency of various sucrose esters was calculated in comparison with the detergent efficiency of sodium dodecylbenzenesulfonate.

From the table, it is obvious that sucrose esters have excellent detergent efficiency as most of them display above 80% detergent efficiency as compared to sodium dodecylbenzenesulfonate and some are even above 90%. The detergent efficiency depends on various factors and some of them are discussed below.

1) Effect of chain length in alkyl group

The percentage of various fatty acids present in the form of triglycerides in different oils, is tabulated in **TABLE 2.2**. This table also includes average chain length and number of double bonds. The fractional numbers in chain length are due to calculation of weight average of each acid present. The method employed is as follows:

The percentage figures of various acids were multiplied by respective number of carbon atoms and the sum total of all these

TABLE 2.1

Surface active properties of sucrose esters prepared from various oils using different methods.

Sr. No.	Expt.No. or code No.	Oil base	Method of preparation for SE	Detergent activity % activity of SE based on Na-DDBSS
1	SE 102 G	Castor	A	88.8
2	SE 120 G	Castor	B	83.7
3	SE 85 G	Castor	B	92.3
4	SE 128	Castor	C	89.5
5.	SE 131	Castor	D	93.7
6.	SE 131 G	Castor	D	85.5
7.	SE 126	Sal	A	86.0
8.	SE 126 G	Sal	A	92.8
9.	SE 122	Sal	C	78.6
10.	SE 118	Sal	D	58.4
11.	SE 148 G	Groundnut	A	91.3
12.	SE 80	Groundnut	B	92.1
13.	SE 147	Groundnut	C	89.4
14.	SE 145 G	Groundnut	D	82.7
15.	SE 33 G	Hydrogenated-vegetable	A	94.9
16.	SE 89 G	Mohwa	B	87.2
17.	SE 74 G	Rice bran	B	73.5
18.	SE 93 G	Pilu	B	82.6
19.	SE 28 G	Coconut	A	62.4
20.	SE 57 G	Coconut	A	67.0

TABLE 2.2

Percentage, average chain length and number of double bonds for different acids in various fats.

Sr. No.	Name of the acid	Pilu oil	Sal oil	Mohwa oil	Rice Bran oil	Groundnut oil	Coconut oil	Castor oil
1	Caproic acid (C_6)	-	-	-	-	-	0.3%	-
2	Caprylic acid (C_8)	-	-	-	-	-	7.5%	-
3	Capric acid (C_{10})	-	-	-	-	-	7.1%	-
4	Lauric acid (C_{12})	32%	-	-	-	traces	49.1%	-
5	Myristic acid (C_{14})	41%	-	-	0.5%	-	15.8%	-
6	Palmitic acid (C_{16})	18.3%	6.5%	21.5%	24.1%	8.3%	9%	-
7	Stearic acid (C_{18})	-	39.8%	22.0%	2.5%	3.1%	2.1%	-
8	Oleic acid (C_{18})	8.0%	41.8%	46%	41%	56%	6.6%	-
9	Linoleic acid (C_{18})	0.7%	2.7%	8.9%	30.7%	26%	1.8%	5.1%
10	Linolenic acid (C_{18})	-	-	-	-	-	-	-
11	Ricinoleic acid (C_{18})	-	-	-	-	-	-	94.9%
12	Arachidic acid (C_{20})	-	9.2%	1.6%	0.5%	2.4%	0.7%	-
13	Behenic acid (C_{22})	-	-	-	-	3.1%	-	-
14	Lignoceric acid (C_{24})	-	-	-	0.7%	1.1%	-	-
15	Average chain length	14.07	18.05	17.6	17.55	18.1	12.9	18.0
16	Notional double bonds	0.094	0.472	0.638	1.024	1.080	0.102	1.051

was divided by 100. Thus, the final figure reflects the effect of various acids on average chain length depending on their actual percentage.

As the oils used in the reactions contain different acids in various percentages and also considering the fact that at least a few oils contain unsaturated acids in large numbers, only coconut, pilu and hydrogenated oils were selected to study the effect of chain length on detergency. The table shows that out of these three oils, pilu and coconut contain a very small proportion of unsaturation and hydrogenated oil [fully hydrogenated groundnut oil] is completely free from unsaturation. From the **TABLE** 2.2, we could see that detergent efficiencies of sucrose esters prepared from coconut oil, pilu oil and hydrogenated oil are in increasing order. The values being 67.00%, 82.6% and 94.9% in comparison with sodium dodecylbenzenesulfonate. The average chain length in these three oils are 12.9, 14.1 and 18.1 respectively. These results clearly establish the fact that there is a marked increase in the detergent efficiency of sucrose esters as the chain length of acid segment increases. However, it seems that the increase in the percentage detergent efficiency is not proportional to the increase in chain length, as there is an increase of 15.6% in the detergent efficiency by increasing chain length from 12.9 to 14.1, i.e. 1.2 carbon atoms and for further increase of another

12.3% in the detergent efficiency an increase in chain length by
4 carbon atoms from 14.1 to 18.1 was required. From the graph
[Fig.2.1], it seems that after a chain length of 17 carbon atoms
the increase in detergent efficiency tapers off indicating that
ideal chain length is 17-18 carbon atoms.

2) Effect of unsaturation on detergency

While considering the effect of unsaturation in carbon chain
on the detergency, the following five oils with similar chain
length were compared. All these oils have about 18 carbon chain
in their acid segment and degree of unsaturation differs widely
from 0.0 to 1.08 (please refer to TABLE 2.3).

However, the degree of unsaturation has only marginal effect
on the detergent efficiency if we compare the results of
hydrogenated, sal and groundnut oils. These three oils have the
degree of unsaturation as 0, 0.472 and 1.08 respectively, but the
detergent efficiency decreased slightly from 94.9 to 92.8 to 92.1
respectively. The lower efficiency in mohwa and rice bran oil
may be attributed more to reduction in chain length than to
degree of unsaturation.

Like unsaturation, substitution of hydroxy group in the acid
chain also seems to have marginal effect on the detergent
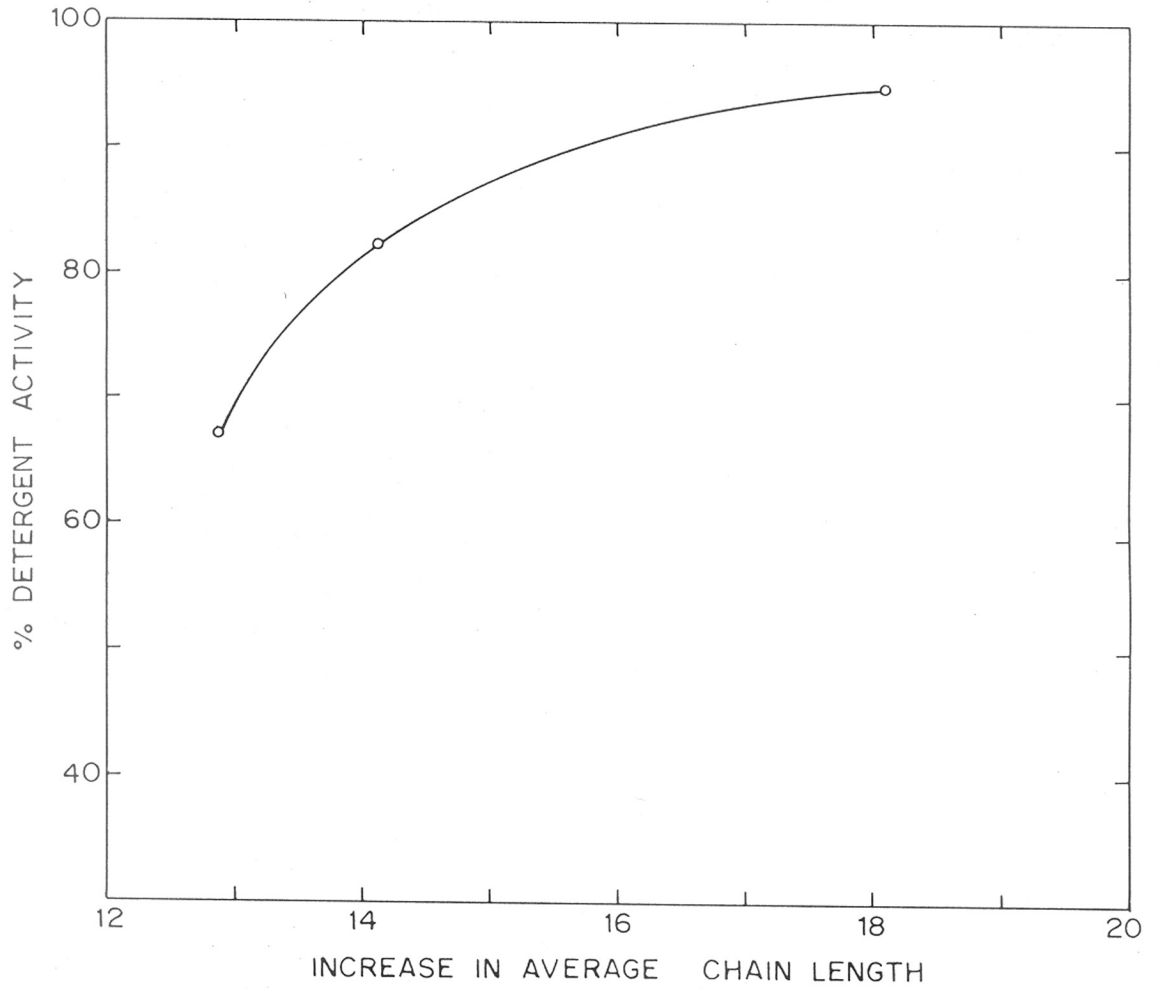efficiency if we compare the results of castor oil and groundnut

FIG.2·1

TABLE 2.3[‡]

Sr.No.	Oil used	Degree of unsaturation	Detergent efficiency	Average chain length
1	Hydrogenated vegetable oil	0.00	94.9%	18.1
2	Sal oil	0.472	92.8%	18.05
3	Mohwa oil	0.638	87.2%	17.6
4	Rice bran oil	1.024	73.5%	17.55
5	Groundnut oil	1.080	92.1%	18.1

‡ [The degree of unsaturation, was calculated by assigning
1/100th part to each percent of mono unsaturated acid,
2/100th part to each percent of unsaturated acids with two
double bonds, 3/100th part to each percent of unsaturated
acids with three double bonds. This is the reason why some oils
with fair percentage of polyunsaturated acids showed degree of
unsaturation above 1.00].

oil. Both these oils have almost similar degree of unsaturation of 1.05 and 1.08 and chain length of 18.0 and 18.1 respectively. Castor oil has one hydroxy group in its acid segment and it was expected to enhance its hydrophilicity and detergent efficiency but the results indicated that there was practically no change in detergent efficiency.

3) Effects of extraction on the detergent efficiency

The comparison of detergent efficiency of 126 and 126G indicated that there was a marked increase in the detergent efficiency after the extraction of the reaction product. This observation was supported by almost all other results where the detergent efficiency of sucrose esters was estimated before and after the removal of unreacted sucrose by solvents. These observations were valid only when sucrose esters were obtained by employing method (A) or method (B). Both these methods involve use of potassium carbonate as a catalyst and that too in catalytic amounts. In the case of methods (C) and (D) involving microemulsion technique sodium stearate was used as a catalyst and that too in substantial amounts. The results of the detergent efficiency of these experiments before and after extraction indicated the opposite trend. This can be observed by comparing the results of 131 and 131G. Here the detergent efficiency of the total reaction product [131] was higher at 93.7% as compared

to the detergent efficiency of extracted product [131G] at 85.5%. In this case, sodium stearate present in substantial quantities helped to boost the detergent efficiency of total reaction product despite the presence of small amount of unreacted sugar. The extraction of reaction product removes sodium stearate and hence, it reduces the detergent efficiency of the reaction product.

B) Surface tension

Surface tension of aqueous solution of various sucrose esters were determined at different concentrations ranging from 0.01% to 0.2% (Please refer to TABLE 2.4). These results were compared with sodium lauryl sulfate and sodium dodecylbenzene-sulfonate at identical concentrations. It may be observed from table 2.4 that the surface tension drops down to about 40 dynes/cm at 0.01% concentration in comparison with water whose value is of the order of 72 dynes/cm, indicating that these compounds are very good surface active agents in general. In fact in some cases, this drop in surface tension is even better than two standard compounds used for comparison.

Critical Micelle concentrations (CMC) of all the compounds mentioned above have also been tabulated in Table 2.4. These values were obtained by plotting a graph of surface tension v/s logarithm of concentration. A few curves have been given in

TABLE 2.4

Surface tension in dynes/cm of the the sucrose esters at different concentrations

Sr.No.	Expt. No. or Code No.	Concentration (wt.%)					CMC values (wt.%)
		0.2%	0.1%	0.05%	0.02%	0.01%	
1	SE 70 X$	33.5	33.7	35.2	37.8	40.4	0.066
2	SE 57 G	29.2	29.4	29.8	31.8	36.7	0.028
3	SE 72 X$	35.6	35.9	35.9	36.3	38.8	0.021
4	SE 74 GP^	33.9	34.5	35.8	37.7	39.7	0.079
5	SE 80	34.9	35.5	36.6	38.1	39.9	0.025
6	SE 76 GP^	33.9	34.3	34.9	36.4	37.9	0.026
7	SE 85 G	36.3	37.0	37.9	38.9	40.7	0.020
8	SE 86 G (castor oil)	34.0	34.2	34.7	37.3	38.7	0.062
9	SE 89 G	36.5	38.4	40.3	43.0	47.2	0.030
10	SE 93 G	34.8	35.2	36.7	38.6	39.3	0.110
11	SLS	38.0	39.6	42.3	43.5	45.8	0.200
12	Na-DDBSS	33.6	33.8	34.6	37.8	40.2	0.059

$ Xylene extract of the total reaction product prepared from coconut oil as per expt. No. SE 70 and SE 72.

^ Isopropanol extract and pet.ether insolubles of the total reaction product prepared from rice bran oil and castor oil as per expt. No. SE 74 and SE 76.

Fig.2.2.   It is clear from table 2.4 and fig. 2.2 that CMC of

most of the compounds lie between 0.02% to 0.06%. This indicates

that the compound to be used for various surface active

properties need not be more than 0.06%. The sharp brake in the

curves depicted in Fig.2.2 indicated the accuracy of the CMC

values.

C) Draves´ wetting test

Wetting power is one of the important characteristics of the

detergents and surface active compounds. In textile processing,

dyeing and variety of other end uses, the surfactants are used to

increase the rate of wetting by aqueous solutions. Draves´

wetting test[8-9] provides a practical means of assessing the

performance of these solutions since it approximates the

conditions of use.   In the standard test, 5g. of skein of

naturally waxed cotton yarn comprising a 54 inch loop of 120

threads, is attached to a 3g. hook and totally immersed in the

surfactant solution by means of an anchor.   The   solution

gradually penetrates the skein which then suddenly sinks.   The

better the wetting the shorter the time required for sinking.

Comparative measurements were made at a fixed temperature and

concentration usually $25^{o}C$ and 0.01% respectively. The results

obtained for some of the sucrose esters are tabulated in TABLE

2.5. From the table, it is apparent that sucrose esters except
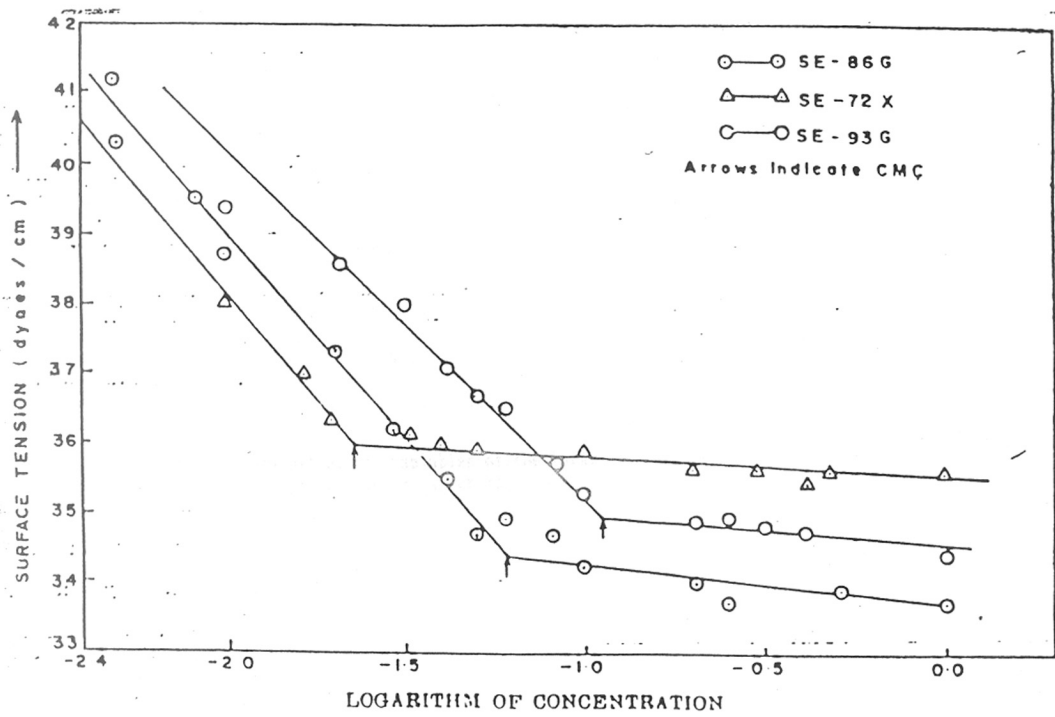
FIG. 2·2

TABLE 2.5

Draves' wetting test at 0.2% concentration for various sucrose esters

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Sr.No. Expt. No. or Code No.   Sinking time

Sr.No.	Expt. No. or Code No.	Sinking time
1	SE 70	More than 4 minutes
2	SE 57 G	148 seconds
3	SE 72	More than 3 minutes
4	SE 74 GP^	More than 3 minutes
5	SE 76 GP^	92 seconds
6	SE 80	More than 5 minutes
7	SE 85 G	More than 3 min. 30 seconds
8	SE 86 G	71 seconds
9	SE 89 G	More than 5 minutes
10	SE 93 G	More than 5 minutes
11	SLS	21 seconds
12	Na-DDBSS	13 seconds

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^ Isopropanol extract and pet.ether insolubles of the total reaction product prepared from rice bran oil and castor oil as per expt. No. SE 74 and SE 76.

those prepared from castor oil are not as good wetting agents as sodium dodecylbenzenesulfonate or sodium lauryl sulfate. The better wetting power of sucrose ester prepared from castor oil as compared to other oils may be due to hydroxyl group present in the acid chain.

D) Foam Height[10]

Foam height and foam stability were tested for some of the sucrose esters and were compared with SLS (sodium lauryl sulphate). The results are tabulated in **TABLE 2.6**. From the results it is quite obvious that sucrose esters except those prepared from coconut oil are very much inferior to SLS as foam boosters. It may be mentioned here that SLS is one of the best foam boosters known. Another observation from these results is that the chain length of the acid segment is one of the most important factors controlling the foaming ability of the detergent and 12 carbon chain as in SLS seems to be optimum number. As has been mentioned earlier coconut oil has an average chain length of 12.9 carbon atoms in its acid segment and sucrose esters prepared from coconut oil give good foam height and foam stability.

E) Emulsification[11]

An emulsion is a dispersion of fine droplets of a liquid within another liquid with which it is immiscible. Emulsion can

TABLE 2.6

Foam height for various sucrose esters at 0.2% conc.

Sr.No.	Expt. No. or Code No.	Foam height (in cms)	Time for ½ height
1	SE 70	9	10 min.
2	SE 57 G	16	More than 2 hrs
3	SE 72	1	-
4	SE 74 GP ^	No foam	-
5	SE 76 GP ^	3	1 min. 45 sec.
6	SE 80	2	5 min.
7	SE 85 G	No foam	-
8	SE 86 G	6	3 min. 5 sec.
9	SE 89 G	2	40 sec.
10	SE 93	1	-
11	SLS	20	70 min.
12	Na-DDBSS	23	65 min.

^ Isopropanol extract and pet.ether insolubles of the total reaction product prepared from rice bran oil and castor oil as per expt. No. SE 74 and SE 76.

either be formed by using suitable surfactant or by vigorous mixing. The emulsions prepared by latter method break quickly by coalescence and phase separation of the internal phase. An emulsifier can significantly reduce the energy required to form an emulsion by absorbing at oil water interfaces (because of its simultaneous solubility in both the phases) where it may reduce the oil water interfacial tension from 20 dynes/cm to <0.1 to 1 dynes/cm. It thus follows that an emulsifier is most effective when its interfacial concentration is at maximum. It should therefore be solvated by each phase but dissolved in neither.

Emulsification ability of sucrose esters was estimated by comparing it with Tween-20 and Tween-80, both are excellent emulsifiers and commercially available. For this purpose two systems were used. The 1st system contains 10% shell oil in water and the 2nd system contains 10% coconut oil in water. Emulsification was carried out at 1% concentration of the surface active agent. Emulsification ability were tested for various sucrose esters. The data of these experiments is tabulated in **TABLE 2.7**. From the data, it is observed that the sucrose esters are very good emulsifiers and are comparable with Tween-20 and Tween-80 which are commercially used.

F) Lime soap dispersant requirement[12]

A lime soap dispersing agent is a material that prevents the precipitation of alkali metal, ammonium or amine salts of fatty

TABLE 2.7

Stability of oil-in-water emulsions at 1% emulsifying agent

Sr.No.	Expt. No. or Code No.	10% Coconut oil-in-water			10% Shell oil-in-water		
		2 hrs	12 hrs	24 hrs	2 hrs	12 hrs	24 hrs
1	SE 70 X (Coconut oil)	1	1	2	1	1	2
2	SE 72 X (Rice Bran oil)	1	1	2	1	2	3
3	SE 74 GP (Rice Bran oil)	1	1	2	1	1	2
4	SE 75 GP -"-	1	1	2	1	2	3
5	SE 76 GP (Castor oil)	1	2	3	1	2	3
6	SE 80 (Groundnut oil)	1	1	2	1	1	2
7	SE 85 G	1	2	3	1	2	3
8	SE 87 G (Castor oil)	1	2	3	1	2	3
9	SE 89 G (Mohwa oil)	1	2	3	1	2	3
10	SE 93 G (Pilu oil)	1	1	2	1	1	3
11	SE 102 G (Castor oil)	1	1	2	1	2	3
12	SE 120 G (Castor oil)	1	1	2	1	2	3
13	SE 128 (Castor oil)	1	2	2	1	2	3
14	SE 131 (Castor oil)	1	1	2	1	2	2
15	SE 131 G (Castor oil)	1	1	2	1	2	2

Sr.No.	Expt. No. or Code No.	10% Coconut oil-in-water			10% Shell oil-in-water		
		2 hrs	12 hrs	24 hrs	2 hrs	12 hrs	24 hrs
16	SE 126 (Sal oil)	1	1	2	1	2	2
17	SE 126 G (Sal oil)	1	1	2	1	2	2
18	SE 122 (Sal oil)	1	1	2	1	2	2
19	SE 118 (Sal oil)	1	2	2	1	2	2
20	SE 148 G (Groundnut oil)	1	1	2	1	2	2
21	SE 147 (Groundnut oil)	1	2	2	1	2	2
22	SE 145 G (Groundnut oil)	1	1	2	1	2	3
23	Tween-20	1	1	2	1	2	3
24	Tween-80	1	2	3	1	2	3
25	Na-DDBSS	1	1	2	1	2	3

Note : 1. Complete emulsification, no creaming
2. Partial coalescence
3. Creaming, no coalescence
4. Emulsion completely broken.

acids by calcium or magnesium ions. In the presence of lime soap dispersants, a hazy dispersion is formed instead of flocculation or precipitation which is a norm if hard water is used for making detergent solution. Lime soap dispersant functions in a physical manner without forming covalent or ionic bonding. A chelating agent or an ion exchanging agent, on the other hand forms chemical bond with calcium, magnesium or other polyvalent ions. A lime soap dispersing agent will thus be effective far beyond the stoichiometric polyvalent cation concentration whereas chelating or ion-exchanging agent will cease to function as soon as the stoichiometric quantity of polyvalent ions have been exchanged.

The cationic surfactants do not possess any lime soap dispersing power. However, anionic and non-anionic surfactants do have some lime soap dispersing ability.

Lime soap dispersing power of sucrose esters was assessed using standard reported methods[13] and the results are presented in **TABLE** **2.8**. The figure expressed in the table, is actually lime soap dispersant requirement for each sample. This is the value in number of grams of surfactant required to disperse lime soap formed from 100 gms of Sodium oleate in water of a hardness equivalent to 333 ppm as calcium carbonate. This implies that lower the value for lime soap dispersant requirement better is the lime soap dispersing power. The results indicate that the

TABLE 2.8

Surface active properties of sucrose esters prepared from various oils

Sr.No.	Expt.No. or Code No.	Oil base	Method employed	Percent lime soap dispersant requirement
1	SE 102 G	Castor oil	(A)	10
2	SE 120 G	Castor oil	(B)	7
3	SE 128	Castor oil	(C)	8
4	SE 131	Castor oil	(D)	7.5
5	SE 131 G	Castor oil	(D)	7
6	SE 126	Sal oil	(A)	7
7	SE 126 G	Sal oil	(A)	7
8	SE 122	Sal oil	(C)	8
9	SE 118	Sal oil	(D)	9
10	SE 148 G	Groundnut oil	(A)	11
11	SE 80	Groundnut oil	(B)	8
12	SE 147	Groundnut oil	(C)	9
13	SE 145 G	Groundnut oil	(D)	9.5
14	Na-DDBSS	-	-	13
15	Span-20	-	-	6
16	Hyoxyd-X100	-	-	9

sucrose esters are better lime soap dispersants than sodium dodecylbenzenesulfonate and are almost equivalent to Span-20 (sorbitanmonolaurate) and Hyoxyd-100 (alkylarylpolyether series) as lime soap dispersants, which are standard non-ionic surfactants.

SECTION – C

EXPERIMENTAL

EXPERIMENTAL

Experimental details of a representative experiment for each of the four methods for the preparation of sucrose esters and also for the preparation of methyl or ethyl esters and catalyst have been described in the following paragraphs along with details of various methods used to determine various surfactant properties.

A) Dry method

This method totally avoids the use of a solvent as a reaction medium and is particularly useful when the end product is meant for either food or pharmaceutical use. Direct use of oil as such, avoiding the preparation of methyl esters is a special advantage of this method. A typical experiment is described below [A finely powdered sugar (80-100 mesh) is required for this type of experiment].

A cylindrical enamel pot (about 2 lit. capacity) containing refined coconut oil (240 g) potassium carbonate (50 g) and a monococoglyceride catalyst (40 g) was heated in an oil bath with stirring to a temperature of 115°C. Sucrose (170 g) was added in small portions over a period of 20 minutes. The reaction mixture which was heterogeneous and very mobile in the beginning gradually became homogeneous, viscous and started swelling due to evolution of carbon dioxide. Finally, the reaction mixture became very viscous and the stirring became very difficult and slow. Apart from these physical changes, the reaction was monitored by solvent extraction method. After regular intervals,

samples of reaction mixture were withdrawn and dissolved in isopropanol/n-butanol to determine the percentage of insoluble matter (unreacted sucrose). The percentage of insolubles decreased from the initial value of about 23% to 7.5% at the end of 13 hours when the reaction was considered to be over. The reaction was carried out for 13 hours at 116-120°C (pot temperature). The total material obtained 436 gms as such has good surfactant properties.

For purification, one extraction using isopropanol is enough to remove unreacted sugar and other impurities. This purification improves the surfactant properties still further. (Insoluble matter 30 gms from 329 gms of reaction product i.e. insolubles in total reaction product can be computed at 39.75 gms, i.e. 9.12%). The percent sodium dodecylbenzenesulfonate (Na-DDBSS) activity went up from 73.28 to 88.1 (Na-DDBSS detergent activity taken as 100%).

Sr.No.	Total inputs		Sr.No.	Total outputs	
	Raw material used	Quantity		Product obtained	Quantity
1	Coconut oil	240 g	1	Sucrose esters (crude)	436 g
2	Potassium carbonate	050 g	2	Loss	064 g
3	Monoglyceride catalyst	040 g			
4	Sugar	170 g			
	Total	500 g		Total	500 g

The losses were mainly due to evolution of CO_2 (theoretically 15.94 g) and due to handling because of very sticky and viscous nature of the reaction product.

Groundnut oil, castor oil, mohwa oil and refined sal seed oil were some of the other oils used for the preparation of sucrose esters by this method.

B) DMF Method

This method consists of reacting methyl or ethyl esters of the fatty acids (prepared from various oils) with sucrose in a suitable solvent medium in the presence of a catalyst.

Sucrose [387 g, 1.13 moles] was dissolved in dimethylformamide (DMF, 900 g) and potassium carbonate (8.0 g) was added alongwith methyl ester of castor oil (123.8 g, mol.wt. 312.0 by sap. value). The reaction mixture was heated with stirring under reduced pressure (80-100 mm of Hg) in a suitable reactor. Methyl alcohol formed during the course of the reaction was removed continuously by distillation. The inside temperature was maintained between 92-97°C and the reaction was monitored by TLC. The absence of the spot corresponding to methyl ester indicated the completion of the reaction. Total time required was 12 hours.

The reaction product (1244.7 g) was divided in two portions. One portion (400.4 g) was concentrated under reduced pressure

(5-40 mm of Hg).   The DMF (222 g) was collected by   distillation.
The   residue   mainly   consisted   of   sucrose   esters   (44.7%)   and
unreacted sucrose (55.3%).

The   remaining   major   portion   (844.3   g)   was   initially
extracted   with pet. ether to remove unreacted methyl esters   and
then   concentrated   to dryness.   The solids   obtained   thus   were
extracted with isopropyl alcohol to separate sucrose esters   from
the unreacted sucrose.

The final computed figures of various constituents are given
below.

Sr.No.	Total inputs		Sr.No.	Total outputs	
	Raw material used	Quantity		Product obtained	Quantity
1	Sucrose	387.0 g	1	Sucrose (recovered)	0264.9 g
2.	DMF	900.0 g	2	Sucrose esters	0231.7 g
3.	Methyl ester of castor oil	123.8 g	3	Methyl ester of castor oil	0004.0 g
4.	Potassium carbonate	008.0 g			
		1418.8 g	4	DMF (recovered)	0950.8 g
5.	DMF	0100.0 g	5.	Isopropyl alcohol	1313.0 g
6.	Pet.ether (60-80)	0705.0 g	6.	Pet.ether (60-80)	0650.1 g
7.	Isopropyl alcohol	1405.8 g	7.	Loss	0215.1 g
	Total	3629.6 g		Total	3629.6 g

{ used for Extraction } (handwritten annotation bracketing inputs 5, 6, 7)

Apart from these two methods two more methods were employed for the preparation of sucrose esters. The methods differ only in the medium used for the reaction. In one case, it is propylene glycol and in th other is water. Both the methods depend on the preparation of microemulsion of sucrose and methyl esters by using sodium stearate in addition to the reaction medium.

C) Microemulsion technique (Aqueous system)

Sodium stearate, water (as a reaction medium) and sucrose were mixed together and heated upto 125°C in a suitable reactor to remove as much water as possible (97 g). Methyl ester and KOH were added and the temperature was raised to 150-155°C and maintained at that level for 30 minutes. The total reaction product was separated in three lots and the major portion (248 g) was extracted with isopropyl alcohol to yield pure sucrose esters (75.1 g) and the rest being a mixture of sucrose and sodium stearate (169 g), which can be recycled in the next experiment.

Sr.No.	Total inputs		Sr.No.	Total outputs	
	Raw material used	Quantity		Product obtained	Quantity
1	Sucrose	200 g	1	Water (recovered)	097 g
2	Water	100 g	2	Sucrose esters (crude)	345 g
3	Sodium stearate	075 g	3	Loss	010 g
4	Potassium hydroxide	002 g			
5	Methyl esters of castor oil	075 g			
	Total	452 g		Total	452 g

D) <u>Microemulsion technique</u> (Propylene glycol system)

In a 2 lit. resin kettle, a mixture of propylene glycol [as a reaction medium (918 g)] sucrose (308.4 g) sodium stearate (165 g) potassium carbonate (1.0 g) and methyl esters of sal seed oil (180 g) was taken. It was heated with stirring to 130-135°C when the solution became clear. After half an hour at 135°C, the propylene glycol was slowly distilled off under reduced pressure (125-140 mm of Hg) over a period of 4.5 hrs.

Sr.No.	Total inputs		Sr.No.	Total outputs	
	Raw material used	Quantity		Product obtained	Quantity
1	Propylene glycol	918.0 g	1	Propylene glycol (recovered)	895.0 g
2	Sucrose	308.4 g	2	Sucrose esters (crude)	600.0 g
3	Sodium stearate	165.0 g	3	Loss	077.4 g
4	Potassium carbonate	001.0 g			
5	Methyl esters of refined sal oil	180.0 g			
	Total	1572.4 g		Total	1572.4 g

The total reaction product showed about 78.6% detergent efficacy as compared to Na-DDBSS.

E) Preparation of intermediates and catalyst

For the above reactions, methyl esters of various oils were prepared and used as one of the reactants in the methods B, C and D. For method A, we had used monoglyceride of coconut oil as a catalyst. The methods employed for their preparation are discussed below.

1) Methyl esters[14]

Castor oil (1960 g), methanol (382 g) and sodium hydroxide (12 g) were mixed in a suitable reactor and refluxed for 4 hours (pot temperature $80\pm2^{\circ}C$) and cooled down to room temperature and left overnight. Usually, such reactions furnish two different layers; the top layer of methyl esters and methanol and the bottom layer consisting of glycerol. However, in this particular case there was no separation of layers and hence, the reaction product was neutralized by adding conc. HCl (30 ml) and water (100 ml). Later, the separated layers were worked up to get methyl esters and glycerol. I.R. (Fig.2.3) and NMR (Fig. 2.4) along with boiling point data clearly establish the purity of esters.

Compound (1) : Methyl ester of castor oil

$[C_{19}H_{36}O_3$ (calculated on the basis that it corresponds to methyl ricinoleate)].

b.p.   : $170-215^{\circ}C/4-5$ mm of Hg.

IR (neat)   : 3480 cm^{-1} (br.), -CH-OH- stretching frequency

1735 cm^{-1} (br.), C=O stretching frequency

1675 cm^{-1} C=C stretching frequency

PMR (CCl$_4$)   : 0.883 δ (br, 3H), CH$_3$ protons

1.26 δ (br, 4H), -CH$_2$- all methylene protons
except allylic methylene protons.

2.1 δ (br, 4H), -CH$_2$- allylic
methylene protons.

3.6 δ (s, 1H), hydroxylic proton exchangeable
with D$_2$O.

5.3 δ (br, 2H), olefinic protons.

Sr.No.	Total inputs		Sr.No.	Total outputs	
	Raw material used	Quantity		Product obtained	Quantity
1	Castor oil	1960 g	1	Methyl esters of castor oil	1967.0 g
2	Methanol	0382 g	2	Methanol (recovered)	0153.0 g
3	NaOH	0012 g	3	NaCl	0019.0 g
4	HCl (conc.)	0035 g	4	Glycerol	0141.6 g
			5	Loss	0108.4 g
	Total	2389 g		Total	2389.0 g
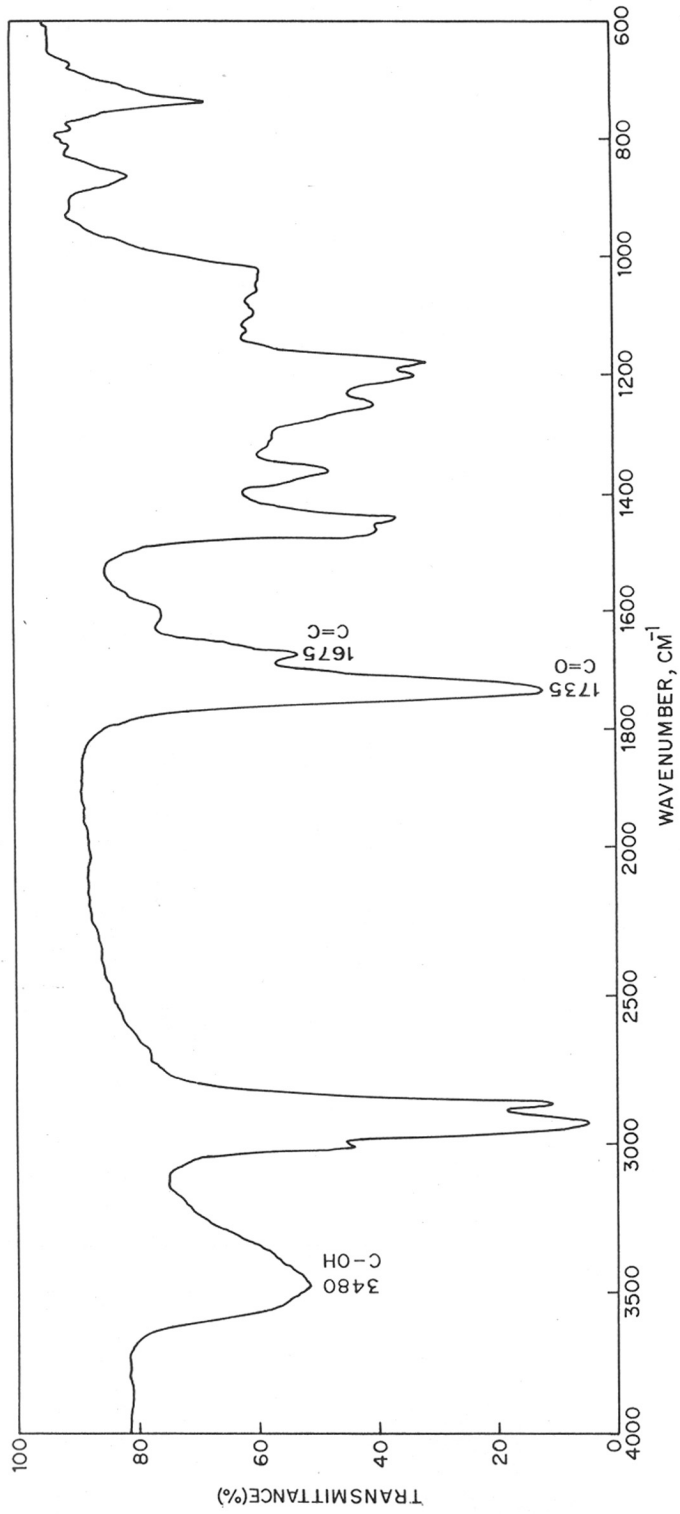
FIG. 2·3 : IR OF METHYL ESTERS OF CASTOR OIL
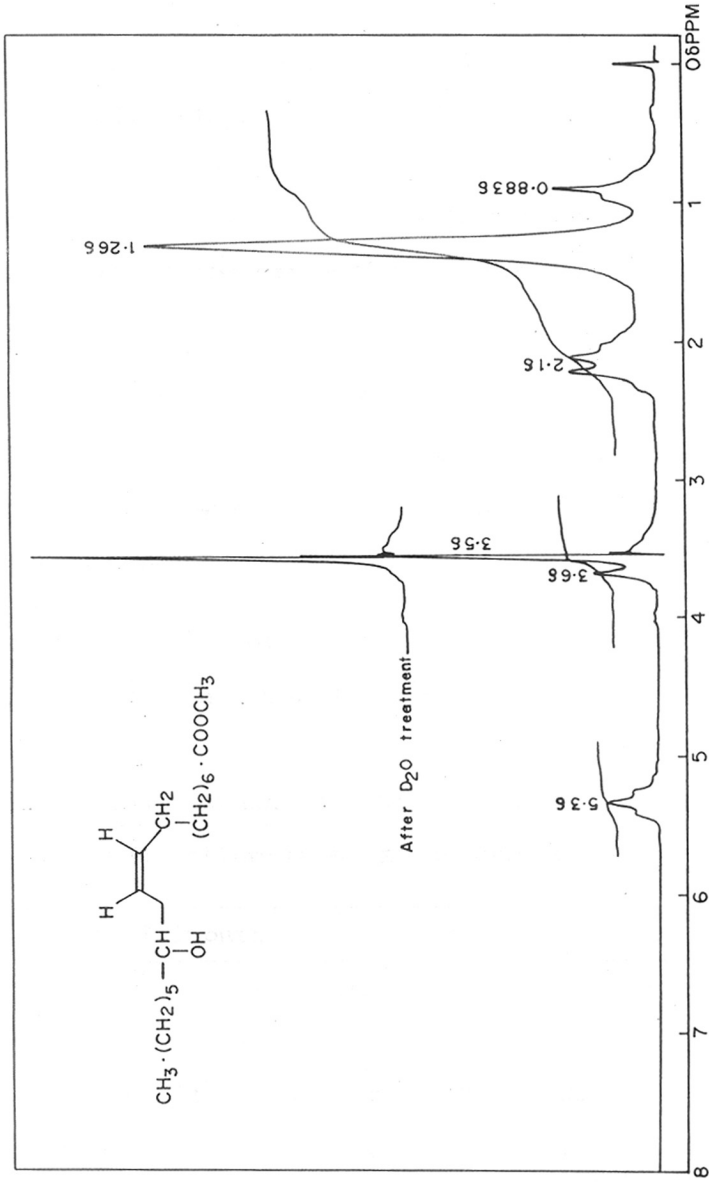
FIG.2·4: NMR OF METHYL ESTERS OF CASTOR OIL

2) Monoglyceride catalyst from coconut oil[15]

Theoretically, this is also a transesterification reaction in which triglycerides from original oil are converted to mono-glycerides by adding more of glycerine. The monoglycerides prepared from coconut oil by a method described below were used as a catalyst in the dry method in the preparation of sucrose esters.

In a four necked two litre R.B.flask, a mixture of coconut oil (800 g), glycerin (389 g) and NaOH (2 g) was taken. The reaction mixture was stirred at 80-85°C for 2 hours under nitrogen bubbling.

The temperature of the reaction mixture was raised to 210-240°C and maintained for 4 hours under inert atmosphere. The reaction product was transferred to a separatory funnel and al-lowed to stand overnight. The top layer gives the required catalyst and the bottom layer gives unreacted glycerine.

Sr.No.	Total inputs		Sr.No.	Total outputs	
	Raw material used	Quantity		Product obtained	Quantity
1	Coconut oil	800.0 g	1	Catalyst	1147.5 g
2	Glycerine	389.0 g	2	Glycerine (recovered)	0030.0 g
3	NaOH	002.0 g	3	Loss	0013.5 g
	Total	1191.0 g		Total	1191.0 g

F) Draves' test for wetting power evaluation

This test consists of finding the sinking time of a 5 g unboiled skein of a gray 2-ply cotton yarn in a solution of the wetting agent. This test was carried out according to the following procedure reported in the literature[8].

A 20 g anchor was attached to a copper wire hook and lead sinker whose total wt. was 1.5 g by a thread 1 inch long. The skein was looped once the anchor and sinker were fastened and the skein was cut open at the other end removing no yarn. The apparatus was dropped into a 50 ml cylinder containing the wetting agent and the time which elapsed between entering and sinking is a measure of the efficiency of the wetting agent. A constant temperature i.e. $25^{\circ}C$ was necessary. The relation between sinking time and concentration was logarithmic. The wetting power was proportional to the lowering of the static surface tension of the wetting agent.

G) Foam Height

a) Construction of the apparatus

The apparatus as shown in the sketch was made to standard dimensions from stock glass. The reservoir or pipette A was filled with the solution to be examined and then placed on the supporting ring at the head of the receiver B which contains 50 ml of the same solution.
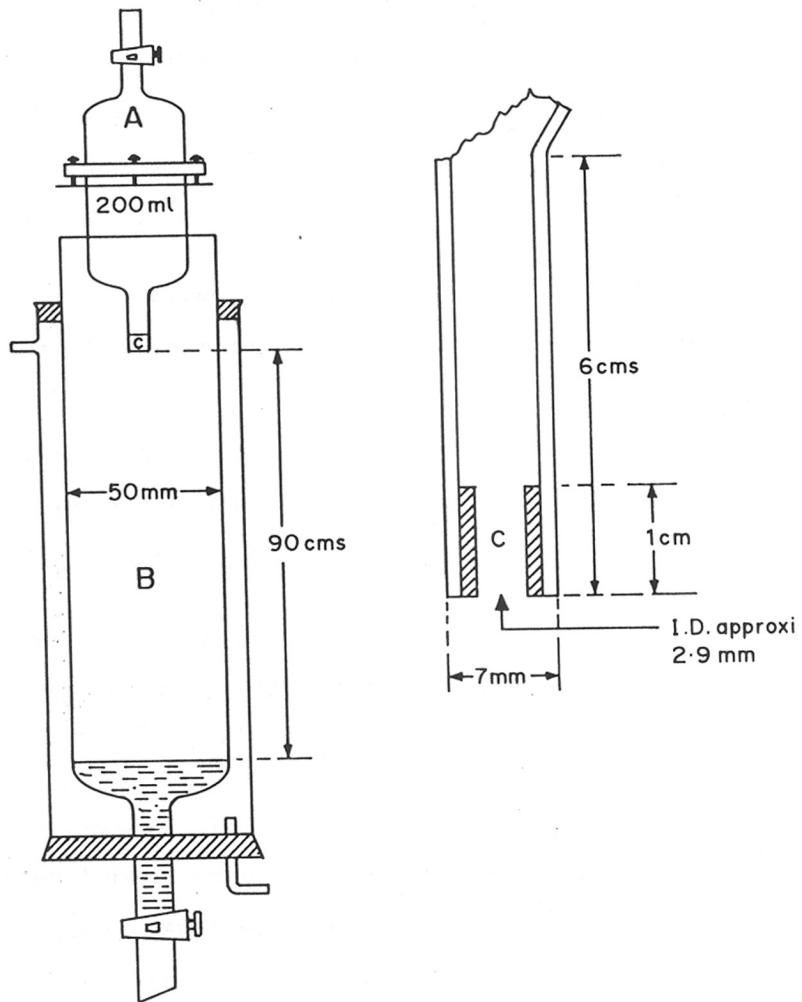
FIG.2·5 : POUR   TEST   APPARATUS

The   stopcock   of   the   reservoir A was   opened   and   as   the
solution   fell through a height of 90 cm foam was formed   in   the
receiver.   It was measured in B immediately after the reservoir A

was emptied. The orifice of A was so constructed that the turbulence set up caused the stream of solution to break up into droplets just after the solution emerged from the orifice. The foam was produced when these droplets struck the surface of the liquid or foam in the receiver.

Extraneous destructive forces and thermal shock were excluded from the system by circulating a liquid of known temperature from a thermostat through the jacket which thus, maintained the liquid and air column at uniform temperature. Evaporation was reduced to a minimum by previous wetting of the receiver walls with the solution.

For convenience in measurement, the height of the foam was read and taken as proportional to the volume of foam formed, assuming that the cylinder is uniform in cross-section.

The reservoir's tip of the pour test apparatus was made up of pyrex glass tubing whose outside diameter is close to 7 mm and length is 6 cms. Another piece of tubing was selected whose diameter is such that it fitted snugly inside the 7 mm piece. From this a short 1 cm section was cut and ground square at both the ends. This inner section was placed flush with the extreme tip of the larger piece and then the outside of the larger tube was heated to redness at one or two points opposite the middle of the inner section. Then the tip assembly is ready to be joined to the reservoir proper.

Orifices which varied in sizes from 2 to 3 mm in internal diameter produced nearly the same amount of foam. However, such variations in orifice sizes need not occur in constructing the apparatus if reasonable precautions were taken. In standardizing several pieces of the apparatus to conform with each other the volume of solution in the reservoir was altered every time slightly.

To set up the apparatus, it was found convenient to use a V-shaped wooden stand in which the pour test apparatus rested upon a shelf and is held in position by metal springs. The wooden stand extended the entire length of the apparatus. At the upper end of the wooden portion the flat annular metal ring was fastened and it is upon this ring that the wooden reservoir holder rested. This arrangement was helpful in aligning the reservoir and receiver as well as protecting the apparatus from breakage.

b) Set up and operation of the pour foam test

1. The receiver was adjusted in such a fashion that it was plumb.

2. The reservoir was adjusted by means of leveling screws so that the stream of water which emerged from the orifice struck the bottom center of the receiver.

3. The stopcock of the receiver was closed and by means of a 50 ml volumetric pipette, 50 ml of the solution was introduced in the receiver. The solution was run down the side wall to

avoid foam formation and to wet the entire interior of the receiver. The tip of the pipette was held against the side wall of the receiver and it was slowly moved around the circumference of the tube so that the solution flowed on all sides.

4. The reservoir was filled in the manner of filling a volumetric pipette. The reservoir was marked at a point which indicated a liquid content of 200 ml.

5. The reservoir was placed in position at the head of the receiver and the reservoir stopcock was opened.

6. When all the liquid ran out of the reservoir the stopwatch was started and the foam height readings were taken immediately and after the foam attained the half of its original volume. The first reading was accepted as standard, however, additional indications of the relative stability of various foams may be obtained in those cases where breakdown occurred in five minutes.

7. The readings were taken as follows :

A millimeter scale was placed behind the receiver so that the zero mark was opposite the point in the receiver which would be reached by the total volume of the liquid introduced into the receiver. The foam production was measured at the top of the column at the highest average height to which the rim of the foam reached. This height was proportional to the volume of the air remaining in the

foam. Additional measurements of the foam height were taken at suitable intervals.

8. The receiver was emptied of the detergent solution while the stopcock was open flushing down the side walls with distilled water until all the foam was swept out of the bottom.

H) Emulsification :

1 gm of sample was weighed out and dissolved in 90 ml of distilled water either by magnetic stirring or by heating on a hot waterbath. After complete clarification of the solution, 10 gms of a hydrophobic chemical substance like groundnut oil, coconut oil or shell oil was added. This mixture was then emulsified by passing it through a hand-homogenizer for about 5 times to get a complete homogeneous suspension, to form an emulsion. This emulsion was transferred to a 100 ml measuring cylinder and emulsion stability was observed by aging the emulsion for 2, 12 and 24 hours.

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CONCLUDING REMARKS

Concluding Remarks

It is intended to present some salient features of the work done towards the preparation of sucrose esters.

1. The work was initiated primarily to assess the feasibility of preparing sucrose esters, with good surfactant properties especially detergent properties, from the abundantly available but very scarcely used tree borne oilseeds of Indian forests. These seeds yield large quantities of non-edible oils which is a renewable resource. It was considered that this will open-up a new outlet for commercial utilization of these oils.

2. Sucrose esters are totally biodegradable and non-toxic. They do not leave any residue in soil or atmosphere to cause any type of pollution.

3. From the results obtained in this study, sucrose esters prepared from these oils can be considered as very good detergents comparable with sodium dodecylbenzenesulfonate, a popular active ingredient of most of the commercial detergents.

4. The sucrose esters prepared by using dry method can be used as emulsifiers and coatings in food and drug preparations and formulations.

5. Sucrose esters are very good emulsifiers for both oil-in-water and water-in-oil system from the emulsion stability

data and their use as drag reducers in petroleum industry can be envisaged.

6. Sucrose esters can also be used as coatings for the preservation of fruits.

7. Sucrose esters cause large drop in the surface tension of aqueous solutions.

8. Sucrose esters are very good lime soap dispersants and hence, detergents based on sucrose esters can be used in hard water also; however, as sucrose esters exhibit less than desired wetting and foaming properties, suitable wetting and foaming agents will have to be added to the detergent formulations based on sucrose esters.

9. From the results it can be seen that sucrose esters prepared from castor oil using microemulsion technique and from sal oil using dry method exhibited very good surfactant properties.

Considering all these results, it is obvious that the present study has conclusively proved that sucrose esters prepared from non-traditional non-edible oils are very good surfactants and can be used primarily as detergents and for variety of other purposes.