Several New Surfactants

Robert B. Steele

Georgeville , Quebec , Canada

June 26 , 2004

Several New Surfactants

Introduction

Surface-active agents – surfactants – are an important industrial chemical commodity . Surfactants are usually classified in either of two general categories . Those that are based on natural sources , the fatty carboxylic acid salts , are **soaps** . Historically , the soaps are the first type of surfactants discovered , manufactured , and used by humans .

The second type of surfactant is the **detergents** . These are made from industrial organic chemicals , usually petrochemicals . They have been "designed" by chemists for specific end-uses , and having certain desirable physical and chemical properties .

Surfactants all have a similar sort of molecular structure , consisting of a water-soluble "head" and a long organic-soluble "tail" . This dual solubilizing nature permits surfactants to simultaneously dissolve in both aqueous and non-aqueous phases . What happens in actual practice is that the predominant liquid phase emulsifies the subordinate phase , which forms a colloidal dispersion in the former liquid . Surfactants , when adsorbed on the surfaces of solids , can cause them to be wetted more readily with either water or organic solvents , and to be dispersed in those liquids .

Chemically , there are four types of surfactants :

- anionic , in which the molecular head has an anionic charge , with an accompanying external cation ; eg. potassium oleate , common soap ;
- cationic , in which the molecular head has a cationic charge , with an accompanying external anion ; eg. cetyltrimethylammonium chloride ;
- nonionic , in which the molecular head is hydrophilic , without having any ionic components ; eg. polyethoxylated lauryl alcohol ; and ,
- amphoteric , in which the molecular head has both anionic and cationic charges attached in close proximity ; eg. certain betaine surfactants , such as hexadecyl–$N^+(CH_3)_2$–CH_2COO- .

Within these four groups , considerable variation is possible in both theory and practice in the two component parts of the surfactant molecules . The hydrocarbon "tail" generally varies in chain length from C8 , octyl , to C18 , octadecyl (stearyl) or octadecenyl (oleyl) . The hydrophilic "head" can consist of various chemical functionalities , such as ,

anionic : sulfonate , $-SO_3-$; sulfate , $-OSO_3-$; and carboxylate , $-CO_2-$;
cationic : quaternary ammonium , $-N^+(CH_3)_3$;
nonionic : polyethoxyl , $-(OCH_2CH_2)_n-OH$;   and ,
amphoteric : acetate , N^+-CH_2COO- ; propionate , $N^+-CH_2CH_2COO-$;
propylsulfonate , $N^+-CH_2CH_2CH_2-SO_3-$; and amine oxide , $N^+(CH_3)_3-O-$.
Chemical feedstocks for many modern detergents can include aromatic ring components , such as benzene and napthalene in the "heads" of the molecules , such as the linear alkylbenzene sulfonates commonly used in laundry detergents . Note than in current practice , the hydrocarbon tails of the surfactant molecules are linear in structure ; it was found that branched-chained tails caused their molecules to be only slowly biodegraded when released into the environment , resulting in unsightly suds and foaming in sewage discharges . The linear-tailed molecules are more quickly and completely biodegraded when released into the environment .

Speaking of the environment , the three main nutrient elements for plant life are nitrogen , potassium , and phosphorus , so modern "environmentally-friendly" or "green" detergent formulations will try to avoid compositions containing these three elements in particular .

For the interested reader I have included a list of surfactant articles and books in ref. 1 , page 20 , that I have found helpful in the study of this particular area of industrial organic chemistry .

In the following brief report I'll discuss the design and synthesis of possible surfactants that are fairly simple and straightforward in their structure and preparation . They will illustrate the concept of the surfactant structure-properties relationship , and might be an enjoyable and educational project for student chemists to investigate , as a sort of practical introduction to surfactants . Related areas of industrial organic chemistry , such as feedstock sources for surfactants , will also be drawn into the discussion .

Phthalic anhydride condensations

In past years I have had some experience with the surfactant systems I'll describe to you . I believe they may be novel materials , or little studied . The interested reader might wish to investigate their novelty in the literature cited in the references and in <u>Chemical Abstracts</u> . In any case , I haven't published any research papers , nor have applied for any patents , regarding the surfactant molecules proposed for investigation below .

After reading about the condensation of 2-octanol with phthalic anhydride , followed by resolution of the phthalate half-ester into its component optical isomers [enantiomers] (ref. 2 , page 21) , I noted the general appearance of the half-ester molecule to that of surfactants in general : a long hydrocarbon tail attached to a hydrophilic head . Would this half-ester actually have detergent properties ? I condensed equimolar quantities of 1-octanol with phthalic anhydride , then neutralized the half-ester with one equivalent of aqueous sodium hydroxide . The resulting product was indeed a nice sudsy , bubbly , "soapy" solution .

It occurred to me that such a surfactant might be of some practical interest , because of the particular structure of the molecule : the sodium carboxylate and ester side-groups are "ortho" to each other on the benzene ring . The bulky ester group might conceivably prevent an exchange of the sodium cation with polyvalent cations , such as calcium , magnesium , and iron found in "hard" , mineralized water .

Generally , the detergents have the distinct advantage over soaps in that their hydrophilic groups , while binding to a certain extent with polyvalent cations in hard water , don't form the undesirable , insoluble "curd" , or "ring-around-the-bathtub" , that the soaps do with minerals . They can be used successfully in hard water , although manufacturers often add "builders" – chemicals that preferentially bind to , and chelate the polyvalent cations – to them so that they will be more effective in hard water .
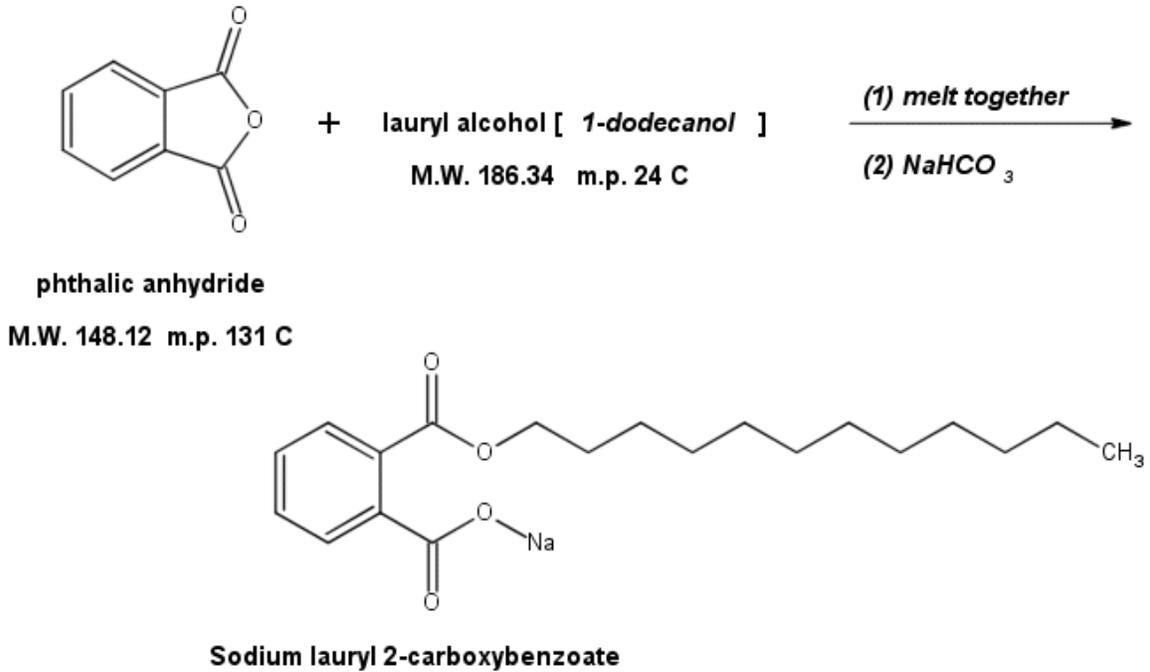
On the other hand , many detergents are considered to be too harsh for use as

personal care surfactants , as with hand and bath soaps , and shampoos . For millennia the soaps have been used for these purposes . The sodium or potassium salts of the fatty carboxylic acids (especially of stearic and oleic acids) have fulfilled the personal washing requirements of humans for ages . Only relatively recently – I would guess in the past half-century or so – have detergents mild enough for personal care use been developed . The betaine surfactants , mentioned earlier , have an application in shampoos , for example , and other detergents are used in hand-washing and bubble bath formulations .

So I wondered if the phthalate half-esters of the fatty alcohols would indeed form curd with polyvalent cations (this , years later !) . Their sodium carboxylate heads should make them mild for personal care use , but at the same time they would be sterically protected by the ortho ester group from bonding with polyvalent cations ; hence , presumably , no curd should form when they are used in hard water .

A series of phthalate half-esters could be synthesized from the condensation of phthalic anhydride – an inexpensive industrial bulk chemical – with the range of fatty alcohols , from C8 (octyl) to C18 (stearyl and oleyl) . A sketch of the anticipated reaction for 1-dodecanol (lauryl alcohol) is shown at the top of the following page , followed by a Table listing the various fatty alcohols commercially available , both as fairly pure research chemicals (eg. from the Aldrich Chemical Company) and in multi-ton quantities , from the primary manufacturers .

As can be readily inferred from the adjective "fatty" , the fatty alcohols have traditionally been derived from the hydrogenation of the corresponding fatty carboxylic acids or their esters . The fatty acids in turn have been produced by the saponification of fats , oils , and greases (which are mostly triglycerides of the acids) into the fatty acid and glycerol . And the fats , oils , and greases have come in copious quantities as waste products from the food processing industry , mostly from the meat packing factories . Since biochemically animals build up fat from acetic acid synthons , the resulting fatty acids all have an even number of carbon atoms : C8 , C12 , C18 , etc.

phthalic anhydride

M.W. 148.12 m.p. 131 C

+ lauryl alcohol [*1-dodecanol*]

M.W. 186.34   m.p. 24 C

(1) melt together

(2) NaHCO $_3$

Sodium lauryl 2-carboxybenzoate

Table 1 : Fatty Alcohols for Surfactant Synthesis

Fatty Alcohol	Mol. Wt.	M.P.	B.P.
1-octanol	130.23 g/mol	- 15 C	196 C
1-decanol	158.29	7	231
1-dodecanol	186.34	24	260
1-tetradecanol	214.39	38	289
1-hexadecanol	242.45	54	179 (10 mm)
1-octadecanol	270.50	60	170 (2 mm)
oleyl alcohol	268.49	6	207 (13 mm)

In recent decades , two new industrial routes to linear fatty alcohols have been developed . The first one , the trialkylaluminum process , produces

fatty alcohols with an even number of carbon atoms , because they are derived entirely from ethylene synthons (ref. 3 , page 21) :

$$n \ Et_3Al \ + \ 3 \ n \ CH_2{=}CH_2 \longrightarrow (Et{-}CH_2CH_2{-})_{3n}Al_n \ .$$
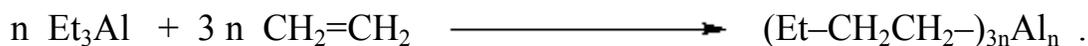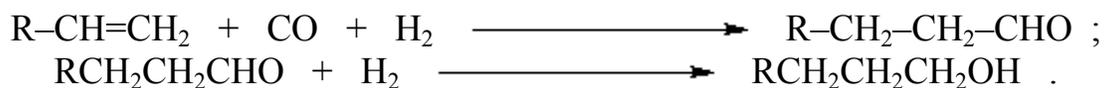
Triethylaluminum is reacted with ethylene gas in steps , extending the chain length of the alkyl group by two carbon atoms at a time . The process can be halted at the desired chain length ; heating the higher alkylaluminum compound with a large excess of ethylene restores the triethylaluminum starting material , and splits off three linear alpha olefin molecules .

Alternately , the enlarged trialkylaluminum product can be oxidized with dry air , then hydrolyzed to yield the corresponding linear higher alcohols , such as the fatty alcohols .

As a brief digression , I was wondering if the higher linear alkylaluminum intermediate could be treated directly with electrophiles to produce surfactant products . Recall that alkylaluminum compounds are somewhat like Grignard reagents ; their carbon atoms bonded to the aluminum atoms are strongly electronegative , and will attack and bond to electrophiles . At the top of the following page is an impromptu Table with several suggested electrophilic compounds that might readily react with , and be inserted into the higher trialkylaluminum molecules . This sort of advanced industrial organic chemistry really wouldn't be suitable for student chemists , toward whom this report , with its simple molecules and chemistry , is oriented .

The second modern source of linear fatty alcohols is the hydroformylation , or "oxo" process , in which the linear fatty alpha olefins referred to above are reacted with carbon monoxide and hydrogen at an elevated temperature and pressure , and in the presence of a suitable catalyst (cobalt compounds are usually used) , to produce an intermediate linear fatty aldehyde . This latter material is hydrogenated to the linear fatty alcohol , which will now have an odd number of carbon atoms :

$$R{-}CH{=}CH_2 \ + \ CO \ + \ H_2 \longrightarrow R{-}CH_2{-}CH_2{-}CHO \ ;$$
$$RCH_2CH_2CHO \ + \ H_2 \longrightarrow RCH_2CH_2CH_2OH \ .$$

Various Proposed Termination Reactions of Aluminum Alkyls

$$(R)_3Al \; + \; 3\,X \xrightarrow{\hspace{3cm}} (R\text{-}X)_3Al \xrightarrow{\;3\;H_2O\;} 3\;R\text{-}XH \; + \; Al(OH)_3$$
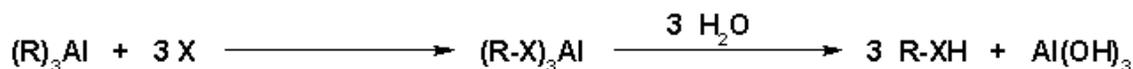
R is an even-numbered alkyl group , from ethyl and higher .

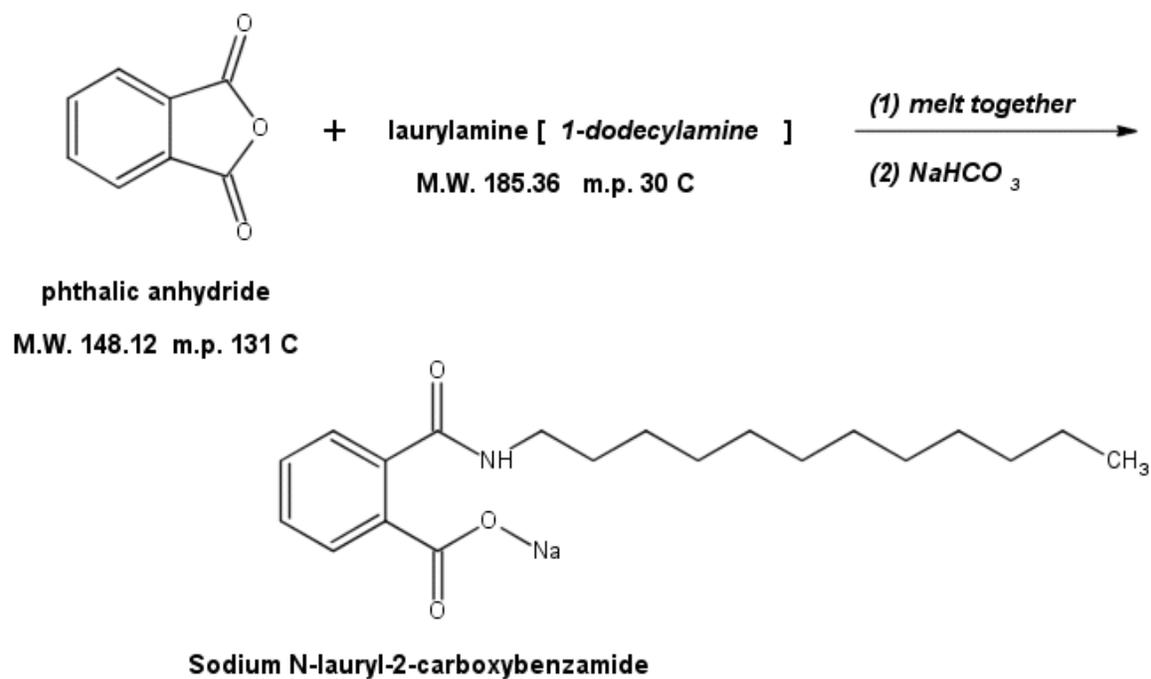X is an electrophile , reacting with the nucleophilic carbon attached to Al .

When X = CO_2 , the product is R-COOH , a carboxylic acid .

X = SO_2 ,	$R\text{-}SO_2H$,	sulfinic acid
X = SO_3 ,	$R\text{-}SO_3H$,	sulfonic acid
X = B-propiolactone	$R\text{-}CH_2CH_2COOH$,	carboxylic acid
X = butyrolactone	$R\text{-}CH_2CH_2CH_2COOH$,	carboxylic acid
X = CH_2=CH-COOEt	$R\text{-}CH_2CH_2COOEt$,	carboxylic ester
X = propanesultone	$R\text{-}CH_2CH_2CH_2SO_3H$,	sulfonic acid

An example of an oxo fatty alcohol would be tridecanol , with thirteen carbon atoms . However , I have listed only the more common , inexpensive even-numbered linear fatty alcohols in Table 1 on page 6 above .

Surfactants based on the ester function seem to be reasonably stable in water solution , at least at neutral pH levels ; for example , Aerosol OT , which chemically is sodium dioctylsulfosuccinate (see page 12 below) . Since amides are generally more resistant to hydrolysis than are esters , the corresponding series of phthalamides might also be investigated .

As with the fatty alcohols , a series of linear fatty amines is also commercially available , both as research chemicals (eg. from the Aldrich Chemical Company) , and in multi-ton quantities from the industrial manufacturers . A similar series of condensations of phthalic anhydride with the fatty amines could be investigated (see the scheme at the top of the following page , and Table 2 , listing a variety of linear primary fatty amines , providing the long hydrocarbon tails for the surfactants) .

phthalic anhydride
M.W. 148.12 m.p. 131 C

+ laurylamine [*1-dodecylamine*]
M.W. 185.36 m.p. 30 C

(1) *melt together*

(2) *NaHCO$_3$*

Sodium N-lauryl-2-carboxybenzamide

Table 2 : Fatty Amines for Surfactant Synthesis

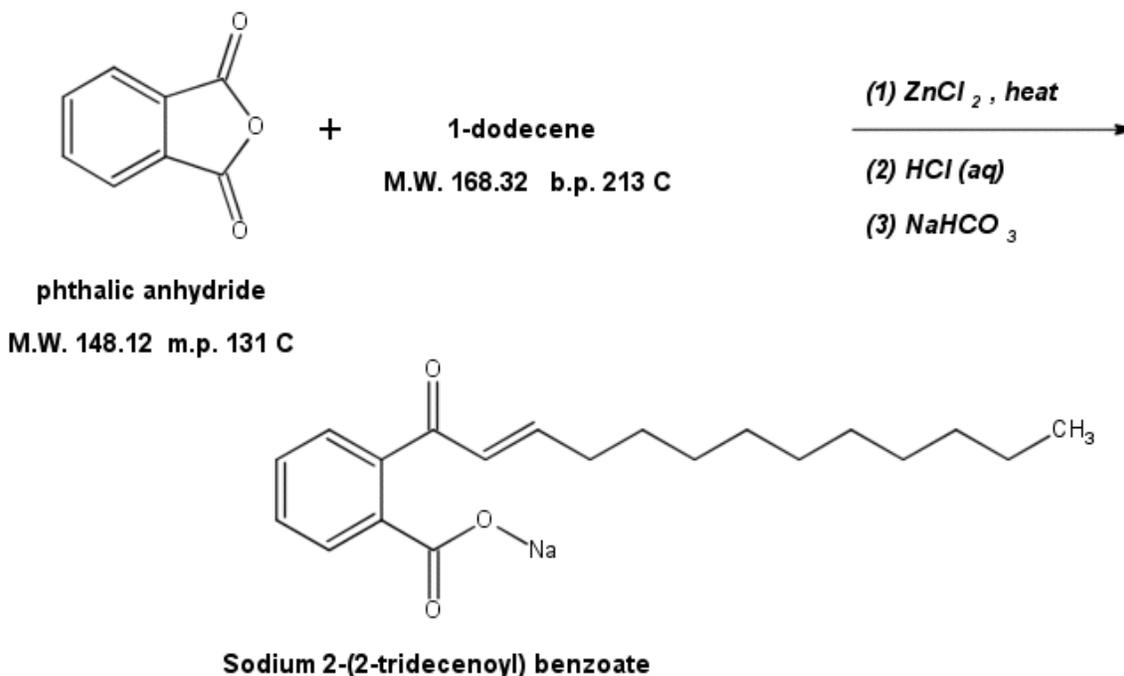| Fatty Amine	Mol. Wt.	M.P.	B.P.
1-octylamine	129.25 g/mol	- 5 C	175 C
1-decylamine	157.30	12	216
1-dodecylamine	185.36	30	247
1-tetradecylamine	213.41	40	162 (15 mm)
1-hexadecylamine	241.46	43	330
1-octadecylamine	269.52	55	n/a
oleylamine	267.50	n/a	n/a
trioctylamine	353.68	n/a	365
triisooctylamine	353.68	n/a	n/a
triisodecylamine	437.84	n/a	n/a
N,N-dimethyloctylamine	157.30	- 57	195

I found an interesting reference to this type of compound in a surfactant textbook (ref. 4 ,) :

"Calcium salts of N-alkylphthalamic acids of formula Ph(COOH)CONHR ,
  where R contains 8 to 20 carbon atoms , are claimed to be valuable
  additives for insecticidal compositions in nonaqueous solutions" .

(U.S. Patent no. 2,554,249 by M.L. Hill , T.L. Cantrell , and H.G. Smith ,
 to the Gulf Oil Corporation) .

Nevertheless , I am under the impression that little research has been carried out on this particular surfactant system . The interested reader should verify its novelty by a thorough literature search , a prerequisite to the organization of any chemistry research program .

It might also be possible to condense linear fatty alpha olefins with phthalic anhydride , in a technique analogous to the Friedel-Crafts reaction :

phthalic anhydride

M.W. 148.12 m.p. 131 C

+   1-dodecene

M.W. 168.32   b.p. 213 C

(1) ZnCl$_2$, heat

(2) HCl (aq)

(3) NaHCO$_3$

Sodium 2-(2-tridecenoyl) benzoate

This sort of acylation of alkyl olefins by anhydrides is a known reaction ;

for example (ref. 5 , page 21) :

b.p. 65 - 69 C (5 mm)

54% yield
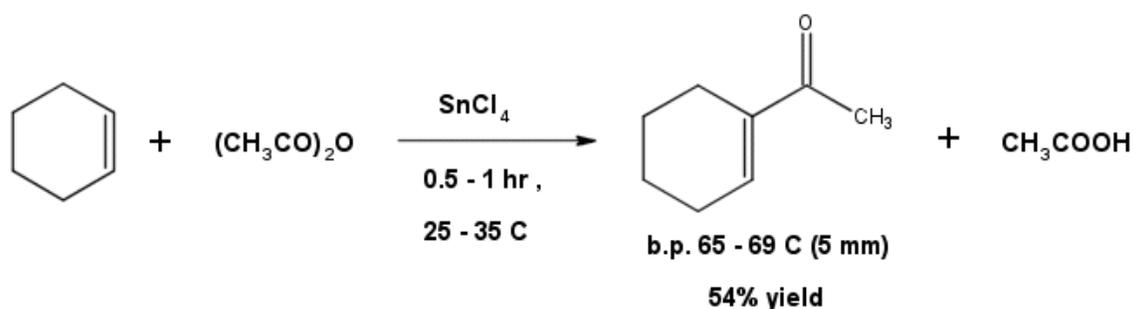
Other researchers have found that anhydrous zinc chloride was the "best" acylation catalyst in their studies of the reaction of acetic anhydride with olefins (ref. 6 , page 21) .

The following Table lists a series of linear fatty alpha olefins for possible investigation in this condensation reaction with phthalic anhydride :

Table 3 : Fatty Alpha Olefins for Surfactant Synthesis

| Fatty Olefin	Mol. Wt.	M.P.	B.P.
1-octene	112.22 g/mol	- 101 C	122 C
1-decene	140.27	- 66	167
1-dodecene	168.32	- 35	213
1-tetradecene	196.38	- 13	251
1-hexadecene	224.43	4	274
1-octadecene	252.49	15	179 (15 mm)

Again , these are the common , "industrial" variety of alpha olefins , which are readily available as either a reasonably pure fine chemical , or in bulk from the primary manufacturer .

As variations of this particular surfactant molecule – assuming , of course that it could be successfully synthesized – it would be interesting to add certain reagents to the reactive α,β–unsaturated bond in the molecule . One such nucleophile that might add to it is the bisulfite anion , HSO_3- . The remarkable surfactant Aerosol OT is manufactured by such a reaction :

Di-n-octyl maleate

Sodium dioctylsulfosuccinate (Aerosol OT ™)
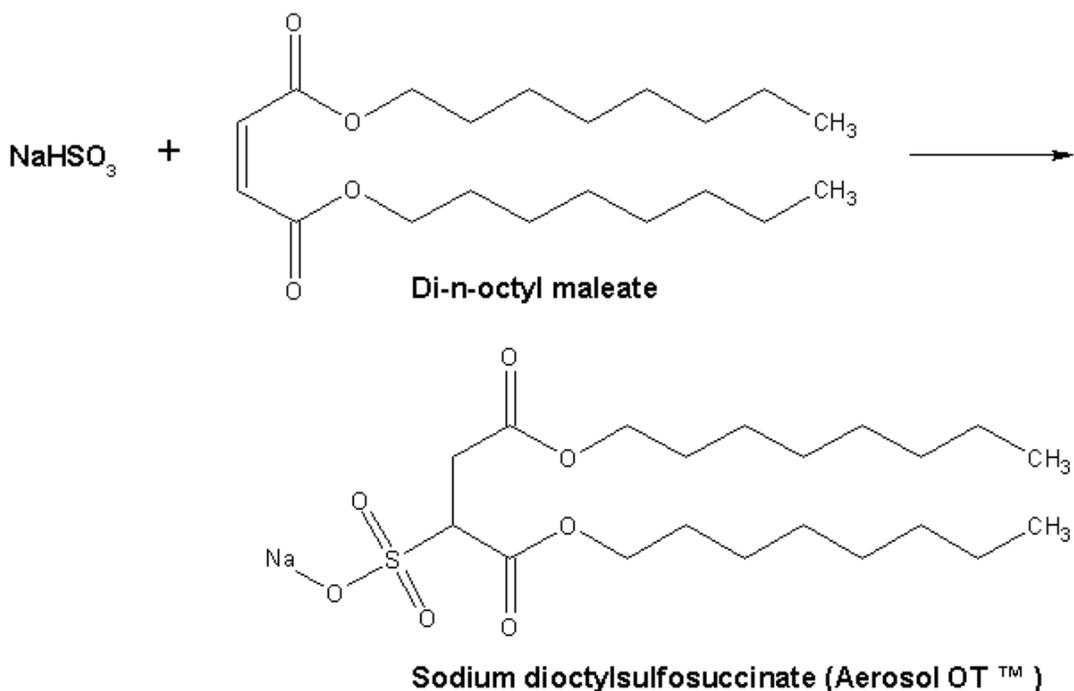
In our case , the derivative surfactant would have both carboxylic and sulfonic hydrophilic heads , which presumably could make it more versatile in its detergency and resulting applications (see the sketch at the top of the following page) .

Finally – with respect to the phthalic anhydride condensations – bromine could add to the olefin bond in the product sodium 2(2-tridecenoyl) benzoate (sketch , page 10) . This is shown in the sketch on page 14 below . My interest in brominated surfactants came from a research paper published almost fifty years ago , describing the "superbubbles" that could be blown from water solutions of sodium 9,10-dibromostearate , prepared from the

Sodium 2-(2-tridecenoyl) benzoate

NaHSO$_3$ (aq)
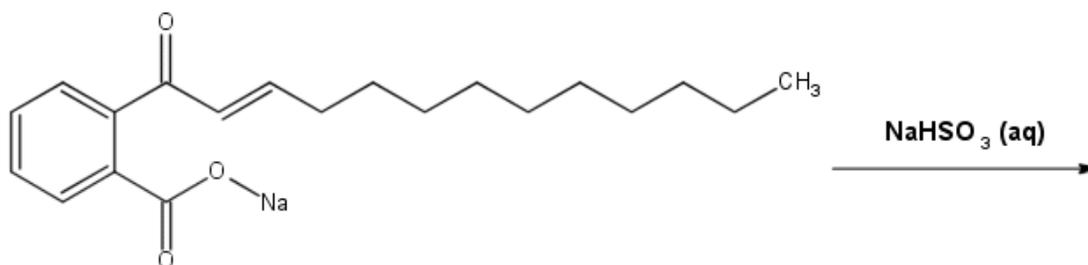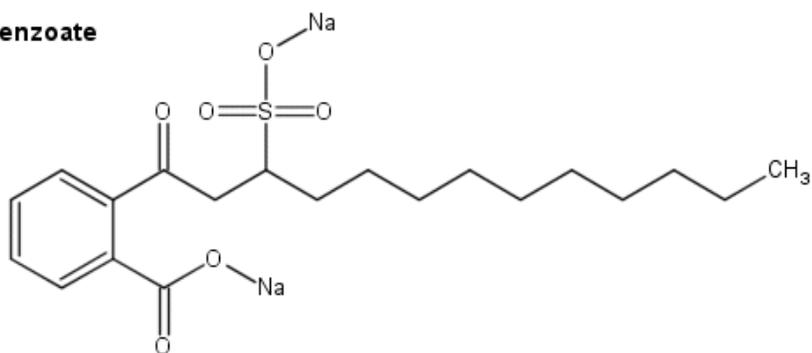
Disodium 2-(tridecanoyl-3-sulfonate) benzoate

addition of bromine to oleic acid (ref. 7 , page 22) . Such bubbles were found to be remarkably stable ; one survived almost seven weeks in a glass jar . Its thickness approximated two monolayers of molecules , and because of a peculiar optical effect , it had a bizarre black appearance . Naturally , it would be very interesting to see if the proposed dibromo phthalate derivative would exhibit similar properties of producing such tenacious black bubbles . It is conceivable that when processed for purification , the adduct could debrominate and cyclize to the lactone :

Sodium 2-(2-tridecenoyl) benzoate

(1) HCl (aq)

(2) Br_2 / CH_2Cl_2

(3) $NaHCO_3$

Sodium 2-(2,3-dibromotridecanoyl) benzoate
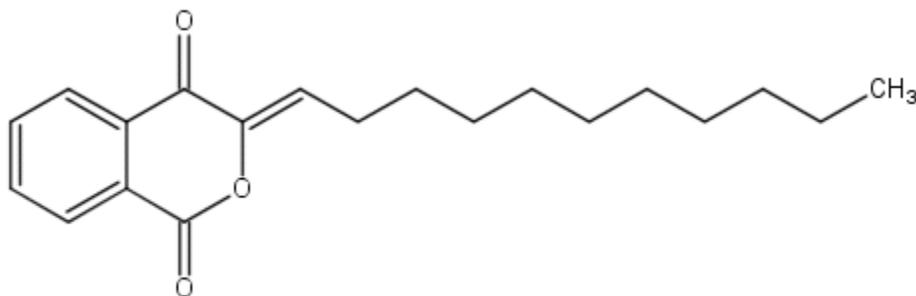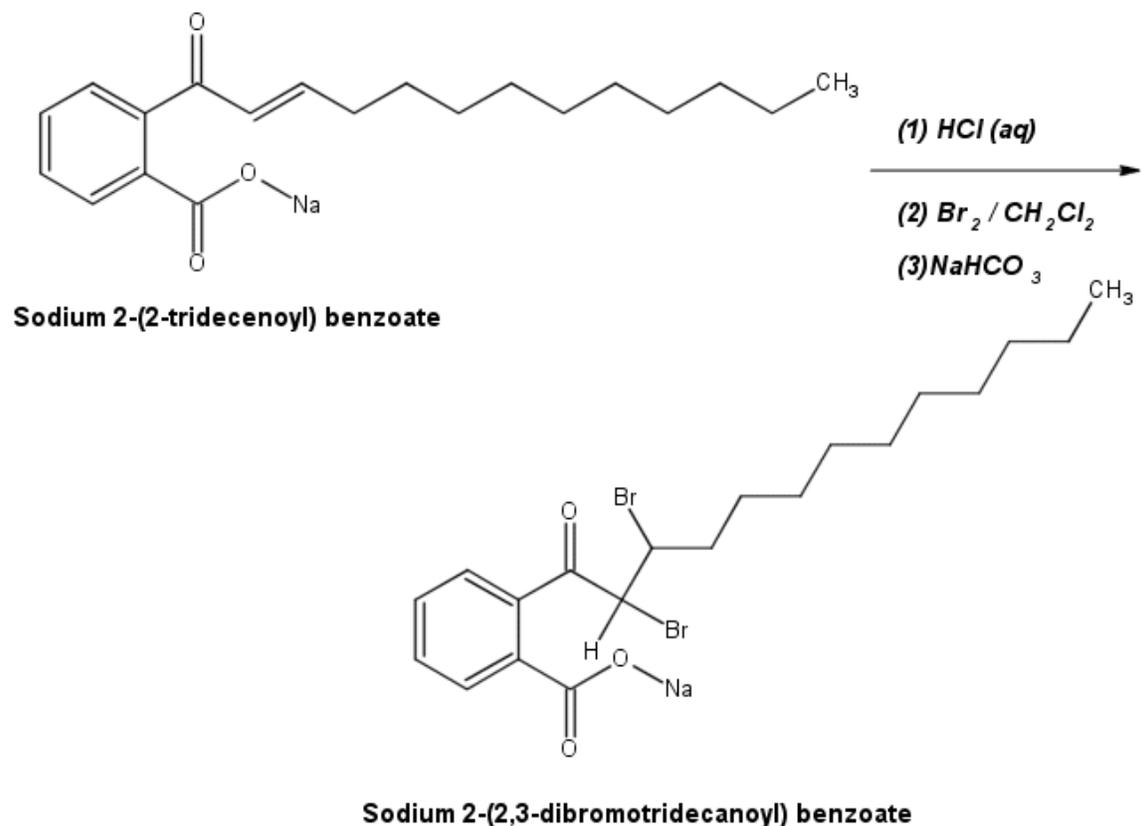
Acyl gemini quaternary ammonium surfactants

Other surfactants I briefly examined some time ago were quaternary ammonium compounds – cationic "quats" – but with an unusual quaternizing agent . Reasonably stable quats were formed by acylating tertiary amines with a difunctional acid halide , phosgene , $COCl_2$.

In the classic von Braun degradation of tertiary amines with cyanogen bromide , the amine is readily dealkylated by the pseudohalogen , with the formation of the residual dialkylcyanamide and the corresponding alkyl bromide :

$$R_3N \ + \ CN–Br \longrightarrow R_2N–CN \ + \ RBr \ .$$

Similarly , it is known that phosgene can efficiently dealkylate a tertiary amine such as trimethylamine :

$(CH_3)_3N + COCl_2 \longrightarrow (CH_3)_2N–COCl + CH_3Cl$.
dimethylcarbamyl chloride
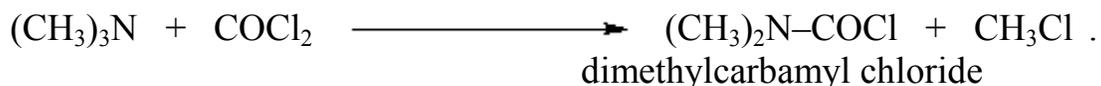
The solid adduct that initially forms upon reaction of the amine and phosgene with cooling in ice has been identified as $(CH_3)_3N^+–COCl$ Cl- ; however , it is quite unstable and decomposes into the carbamate and methyl chloride at ambient and higher temperatures (ref. 8 , page 22) .

This reaction seems to be a general one for low molecular weight tertiary amines . What about the fatty amines , though ? The decomposition of the transient adduct must occur by the nucleophilic attack of the chloride anion on one of the pendant methyl – or generally , alkyl – groups . Chloride is a rather feeble nucleophile in any case ; and if one or more of the alkyl groups is very large (as in a fatty amine) , steric hindrance about the carbon atoms bonded to the quaternized nitrogen atom will effectively curtail any removal of the alkyl group by the ineffective chloride anion . In the case of the fatty tertiary amines , with at least one of the alkyl groups C8 to C18 in length , the adduct of two equivalents of amine with one equivalent of phosgene should be thermally stable , at least at ambient temperature :

solvent
eg. 2 lauryl–$N(CH_3)_2$ + $COCl_2$ $\longrightarrow$
lauryl–$(CH_3)_2N^+$–CO–$N^+(CH_3)_2$–lauryl $(Cl-)_2$.
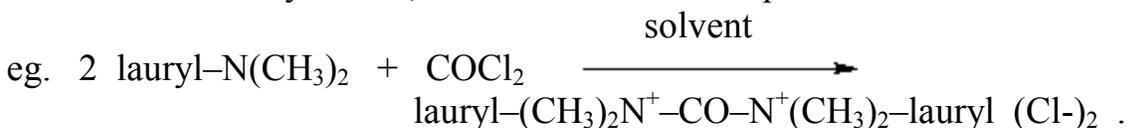
Note that the proposed acyl quat is a urea derivative , 1,3-dilauryl-1,1,3,3-tetramethyluronium dichloride .

I carried out a number of simple "beaker" experiments with a selection of fatty tertiary amines , the Armeens (DM12D , DM16D , DM18D , and DMOD , where "DM" stands for dimethyl , 12 is for the hydrocarbon chain length in carbon atoms , and the terminal "D" indicates a distilled , and hence reasonably pure grade of the product . The "O" stands for the oleyl product , that is N,N-dimethyl-N-oleyl [octadecenyl] amine) . The addition of phosgene gas bubbling into the solution of the amine in ethyl ether at

room temperature produced a snow-white , voluminous precipitate of adduct in the form of a slushy slurry which proved to be rather difficult to separate on a sintered glass filter . Nevertheless , high yields (80% to near quantitative) were obtained of stable , water-soluble solids in these experiments . Sudsy , detergent-like water solutions were produced by the adducts . The solids were all quite hygroscopic , deliquescing in the humid summer air of the laboratory when left exposed overnight .

I must report a rather unpleasant experience with the phosgene gas . This chemical was used as a toxic agent in artillery shells in World War I , and I was unfortunate enough to experience the same sort of choking effects as the soldiers exposed to phosgene at that time . I was trying to rotoevaporate the solvent from the reaction slurry , not realizing that the excess phosgene was escaping from the water pump in the sink , which was providing a partial vacuum in the flask . I was under the impression that phosgene more or less instantly hydrolyzed when dissolved in water , but this proved to be false . It seems that the chlorinated phosgene molecules are actually somewhat water repellent , and they only slowly hydrolyze . Meanwhile , both the laboratory and me were filling up with phosgene ……most unpleasant !

Therefore , I must again repeat my "standard warning" to researchers investigating any of the chemistry discussed in this report :

I cannot overemphasize the great need for **safety** if the following procedures – and any others mentioned in this text – are carried out . The reader must assume full responsibility for the safe manipulation of the reagents cited and in carrying out any actual trial runs . Of course , I expect all my readers are mature , responsible chemists , and are well versed in chemical theory and practice . As a basic minimum precaution , however , I would suggest that no more than semi-micro quantities of reagents (a gram or less) be utilized , that the experiments be carried out in a clean , vacant area with air aspiration (an empty fume hood) , and that protective equipment be deployed by the researcher , **especially** eye protection (the latter I can personally certify !) .

The fatty amines mentioned in this study are all rather innocuous chemicals , but the dichloro acylating reagents , such as phosgene , are all highly

reactive electrophiles . As such , they are toxic , hazardous compounds , and must be handled very carefully by knowledgeable personnel . Good laboratory technique and housekeeping are essential with these chemical reagents .

In addition to the N,N-dimethyl-fatty amines , I have listed in Table 2 above on page 9 several more interesting candidate tertiary amines , such as triiosoctylamine . While having shorter hydrocarbon chain lengths than lauryl , cetyl , stearyl , and oleyl , they have three quite substantial hydrocarbon chains per molecule . As such , they should be even more resistant to von Braun degradation than the dimethyl amines , and should be more thermally stable than they are .

This raises another question : are the acyl quats stable with respect to solvolysis , such as hydrolysis ? I didn't investigate this aspect :

$$[R(CH_3)_2N^+]_2CO\ (Cl\text{-})_2\ +\ H_2O\ \longrightarrow\ 2\ R(CH_3)_2NH^+\ Cl\text{-}\ +\ CO_2\ (g)\ .$$
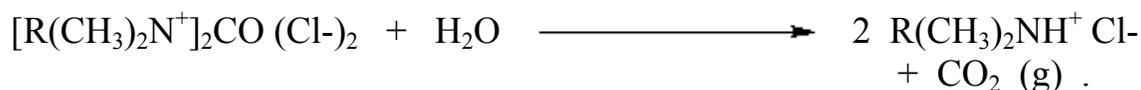
I also didn't carry out physical tests on the quat products , such as CMC (critical micelle concentration) , surface tension , viscosity , wetting , foaming , etc. ; the interested reader is referred to the textbook , review , and research literature cited in the references on pages 21- 22 below , in which the physical properties and testing of surfactants are discussed .

Additional possible acylating agents for the fatty amines are shown in the sketch at the top of the following page . I briefly looked at sulfuryl chloride in my beaker experiments ; it also provided a high yield of stable solid adduct . Sulfuryl chloride is better known as a chlorinating agent in organic syntheses ; however , no chlorination was noted in my simple experiments .

A rather interesting chemical effect might be observed with these new acyl quats . In ordinary amides , an electron resonance can occur between the lone pair of electrons on the nitrogen atom and the carbonyl group . However , in the acyl quats , the lone pair is bonded to an alkyl group , so no characteristic amide resonance is possible . Thus , the carbonyl group in the
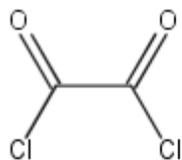
oxalyl chloride

M.W. 126.93 b.p. 63 C
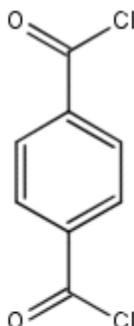
terephthaloyl chloride

M.W. 203.02 m.p. 79 C
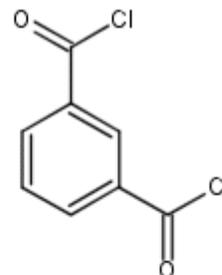
isophthaloyl dichloride

M.W. 203.02 m.p. 43 C
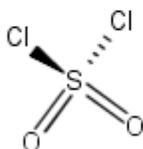
sulfuryl chloride

M.W. 134.97 b.p. 68 C
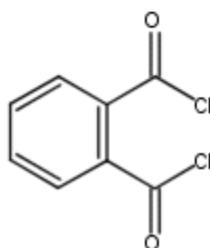
phthaloyl dichloride

M.W. 203.02 b.p. 269 C

in the quats should behave more like that of ketones than amides . This might be observable spectroscopically . For example , the infrared maximum for the phosgene quats should occur at in the ketone region at around 1715 cm^{-1} , rather than in the amide region at around the usual 1650 cm^{-1} (ref. 9 , page 22) .
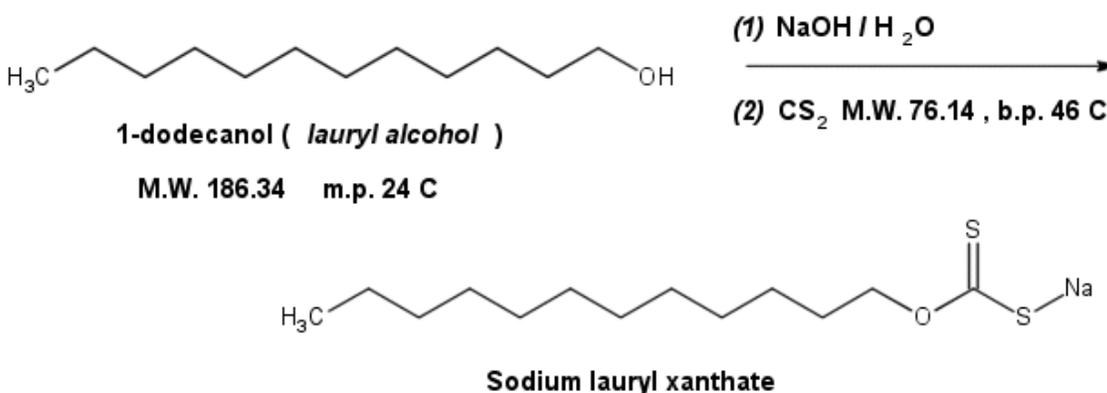
The quats might react with all the classic organic reagents for making identification derivatives of aldehydes and ketones , such as hydroxylamine hydrochloride , semicarbazide hydrochloride , and 2,4-dinitrophenylhydrazine . The bis-oximate of the oxamide quat (from oxalyl chloride and a fatty tertiary amine) might conceivably form a planar coordinate covalent compound with nickel(II) , analogous with the well-known nickel bis(dimethylglyoximate) , Ni(DMG)$_2$, familiar from gravimetric analyses in analytical chemistry .

A final comment on the term "gemini" , which might be applied to these new acyl quaternary surfactants : conventional surfactants have a single

head and tail ; gemini surfactants have two heads and tails , joined together near the "necks" of the molecules , thus forming a sort of "Siamese twin" molecule [gemini = twin , Latin] . For a nice review of gemini surfactants , see ref. 10 on page 22 . Apparently gemini surfactants have some advantages in their physical properties , compared to conventional "single chain" compounds .

Xanthate surfactants

I also carried out brief , exploratory tests preparing fatty alcohol xanthates and seeing if they had detergent properties . Generally , xanthates can be synthesized by reacting together an alcohol , alkali (usually sodium hydroxide) and carbon disulfide . If a linear fatty alcohol (Table 1 , page 6) is used in this process , the xanthate may have surfactant properties :

1-dodecanol (*lauryl alcohol*)

M.W. 186.34   m.p. 24 C

(1) NaOH / H$_2$O

(2) CS$_2$ M.W. 76.14 , b.p. 46 C

Sodium lauryl xanthate

In several simple "beaker" experiments quite some time ago (early 1970s , if memory serves) , I found that the xanthates prepared by a simple blending of the three components did indeed produce soapy , sudsy water solutions . Xanthates of lower alcohols are used commercially as mineral wetting and flotation agents in the mining industry (ref. 11 , page 22) , so this discovery really isn't too surprising . I'm not sure of the novelty of this proposal , so the interested reader should carry out a thorough literature search on the subject before committing to a research project on it .

It might also be possible to use linear fatty amines in place of the alcohols ,

to produce the corresponding N-xanthates ; for example ,
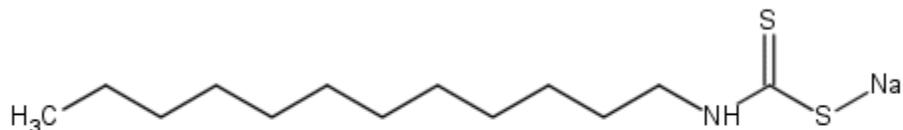
Sodium N-lauryl amidoxanthate

These latter compounds might be more resistant to hydrolysis than their oxygenated counterparts , especially in low pH conditions (the O-xanthates decompose very quickly into the alcohol and CS_2 when exposed to acids ; this is the basis of the "viscose process" , in which the water-soluble cellulose xanthate is extruded in fine threads into an acid bath . The regenerated cellulose fibers are used as rayon in textiles . The film equivalent became cellophane , a familiar packaging material) .

I cannot emphasize too strongly the need for caution when using carbon disulfide either as a reagent , as with the xanthates , or as a solvent . It is **extremely flammable** (and toxic , and foul smelling) . Like ethyl ether , it has a low flashpoint , and can be ignited even by a hot surface . It should be handled and used only in a fume hood , with good ventilation , and in the complete absence of flames , sparks , or hot surfaces . Be very careful disposing of "spent" carbon disulfide , too .

References

1. An exhaustive listing of hundreds of classes and individual surfactants by chemical name and by trade name is provided in McCutcheon's Detergents and Emulsifiers , MC Publishing Co. , McCutcheon Division , 175 Rock Road , Glen Rock , NJ 07452 ; web page at http://www.gomc.com/mccutcheons/index.html ; A. Cahn and J.L. Lynch Jr. , "Surfactants and Detersive Systems" , Kirk-Othmer Encyclopedia of Chemical Technology [KOECT] , vol. 22 , pp. 332-432 , M. Grayson and D. Eckroth (eds.) ,

John Wiley , New York , 1983 ;
M.J. Schick (ed.) , <u>Nonionic Surfactants</u> , Surfactant Science Series vol. <u>1</u> , Marcel Dekker , New York , 1967 ;
E. Jungermann (ed.) , <u>Cationic Surfactants</u> , Surf. Sci. Series vol. <u>4</u> , Marcel Dekker , New York , 1970 ;
W.M. Linfield (ed.) , <u>Anionic Surfactants</u> , Surf. Sci. Series vol. <u>7</u> , parts 1&2 , Marcel Dekker , New York , 1976 ;
H.A. Wittcoff and B.G. Reuben , <u>Industrial Organic Chemicals in Perspective</u> , Part 2 , <u>Technology , Formulation , and Use</u> ; Ch. 7 , "Surface Active Agents" , pp. 182-212 ; John Wiley , New York , 1980 ;   and ,
M.J. Rosen , "Surfactants : Designing Structure for Performance" , <u>Chemtech</u> <u>15</u> (5) , pp. 292-298 (May , 1985) .

2.   B.S. Furniss et al. , "Resolution of (±) Octan-2-ol" , <u>Vogel's Textbook of Practical Organic Chemistry</u> , 4th ed. , Longman , London , UK , 1978 ; pp. 578-580 .

3.   P. Wiseman , <u>An Introduction to Industrial Organic Chemistry</u> , 2nd ed. , Applied Science Pubs. , London , UK , 1979 ; production of alpha-olefins by paraffin wax cracking , p. 77 ; by the Ziegler oligomerization of ethylene with triethylaluminum , pp. 268-270 ; oxidation and hydrolysis of higher alkylaluminums to fatty alcohols , ibid.

4.   A.M. Schwartz , J.W. Perry , and J. Berch , <u>Surface Active Agents and Detergents</u> , vol. <u>2</u> , Interscience , New York , 1958 ; p. 38 .

5.   E.E. Royals and C.M. Hendry , "The Acylation of Olefins . I . The Acetylation of Cyclohexene" , <u>J.Org. Chem.</u> <u>15</u> (6) , pp. 1147-1154 (1950) .

6.   A.C. Byrns and T.F. Doumani , "Ketone Synthesis , The Condensation of Acid Anhydrides With Olefins" , <u>Ind. Eng. Chem.</u> <u>35</u> (3) , pp. 349-343 (1943) .

7. A.L. Kuehner , "Long-lived Soap Bubbles , The Use of Sodium 9,10-Dibromostearate Solutions" , <u>J. Chem. Educ.</u> <u>35</u> (7) , pp. 337-338 (1958) ; see also an earlier paper of his on this subject of durable soap bubbles , idem. , "New Tough Films and Bubbles" , <u>J. Chem. Educ.</u> <u>25</u> (4) , pp. 211-212 (1948) . Glycerol was used as a humectant to prolong the lifespan of soap bubbles .
Kuehner (pronounced "Keener") was a professor of chemistry at Bishop's University , Lennoxville , Quebec , Canada , where I attended school (before my time there , though) . The story has it that he would blow a huge , iridescent soap bubble at the beginning of his lecture , delighting his student chemists , and the bubble would still be intact at the end of the hour-long instruction .

8. V.A. Rudenko , A. Ya. Yakubovich , and T. Ya. Nikiforova , "Splitting of Tertiary Amines , Analogous to the Braun Reaction" , <u>Chem. Abs.</u> <u>42</u> , 4918f (1948) . See also ,
ibid. , <u>70</u> , 28207s (1969) ;
ibid. , <u>41</u> , 1214i (1947) ;
ibid. , <u>48</u> , 1964d (1954) ;
ibid. , <u>53</u> , 21813e (1959) ;
ibid. , <u>52</u> , 6155h (1958) ;
ibid. , <u>84</u> , 42634z (1976) ;
ibid. , <u>89</u> , 41896c (1978) ; and ,
ibid. , <u>101</u> , 229658x (1984) .
These abstracts all refer to papers describing the reaction of phosgene and other electrophilic acylating agents with tertiary amines .

9. K. Nakanishi , <u>Infrared Absorption Spectroscopy , Practical</u> , Holden-Day , San Francisco , CA , 1964 ; pp. 42-46 .

10. M.J. Rosen , "Geminis : A New Generation of Surfactants" , <u>Chemtech</u> <u>23</u> (3) , pp. 30-33 (March , 1993) .

11. G.H. Harris , "Xanthates" , <u>KOECT</u> [ref. 1 , page 20] , vol. <u>24</u> , pp. 645-661 (1984) . Fatty alcohol xanthates weren't mentioned .