

Application of ^{13}C NMR to the Identification of Surfactants in Mixture

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The possibility of using the ^{13}C NMR technique as a preliminary screening for the analysis of manufactured household products is presented. Spectra for several surfactants and related products in water solution were obtained for reference. The application of ^{13}C NMR to commercial products shows that many surfactants can easily be distinguished from one another and determined from a single spectrum without laborious separative pretreatments.

The complete analysis of commercial detergents is becoming more and more difficult as the complexity of formulations increases. Nowadays, a wide range of manufactured products usually consists of different ionic and nonionic surfactants and a variety of other organic and inorganic constituents. Completely identifying the various components of a modern detergent product can be a very complex task. As a rule, it is necessary to effect separation. The analysis procedures most commonly used are extraction procedures, followed by column chromatography and then by chemical analyses of the various fractions (1-3). None of these procedures, however, is uniformly applicable, and it may be necessary sometimes to proceed by trial and error, at the expense of time. The procedure which the analyst will adopt depends upon whether the presence of certain surfactants is known or unknown. In other words, a better organized approach to the analysis can certainly be planned if one can have advance information on the nature of the mixture of surfactants present in the product under examination. This kind of information, in addition, may be all that is required. In specific market surveys a complete analysis of the components may not be necessary, but the combination of the various surfactants must be continuously and rapidly checked.

The application of instrumental methods could furnish an answer to this problem. However, the function of instrumental methods usually has been for identification after qualitative separations have been achieved. Chromatographic techniques, such as TLC and HPLC, certainly have been used to determine surfactants in commercial detergents (4-6). These techniques are not always suitable for quantitative analysis though. They often require a long time to optimize conditions of analysis and cannot be applied indifferently for any detergent.

In the present work the possibility of using ^{13}C FT NMR as a useful analytical tool in the field of detergent is considered.

We are routinely applying this technique already as a preliminary screening for the analysis of manufactured products. The high resolution of the technique, by contrast with other instrumental methods, allows one to get useful information without any laborious separation,

working directly with the commercial product, if liquid, or simply with an ethanol extract, if powder. One can determine rapidly (usually no more than ca. three hr of repetitive scans) not only the nature of the surfactant mixture, but also useful information on structure and on the presence of other organic and inorganic constituents. Of course the amount of information one can get from a single ^{13}C NMR spectrum of a detergent depends on the extent of experience gained in the application of the technique, examining both standard samples and commercial products. In this study information from the ^{13}C NMR examination of several standard surfactants as samples, of various related organic and inorganic constituents, and of different commercial products, is presented. The work, in addition, is a useful compendium, particularly for anionics and nonionics, of the chemical shift assignments which can be of practical value for NMR spectroscopists dealing with surfactants.

EXPERIMENTAL

Materials. Several surfactants and some related constituents were used as standards in this study. Their chemical structures and abbreviations are illustrated in Table 1. In the case of LAS, products of different industrial origin were used, with linear alkyl chains in the 10-13 carbon range produced via HF or via AlCl_3 . The alcohol derivatives such as AS, AES and AE were also industrial products, where the parent alcohol had either a linear structure (natural alcohols) or a branched structure (synthetic oxo-alcohols) mainly in the 10-15 carbon range. Oxo-alcohols of different processes, i.e. Ugine Kuhlmann and Shell processes, were considered.

SAS and AOS were industrial products obtained from Hoechst (Germany) and Witco (France), respectively, and were used without further purification. For these products some of our samples, prepared and purified in the laboratory, also were considered. MES was our laboratory product. CDE and QUAT were commercial products from Marchon (Italy) and Rewo (Germany), respectively. NTA and EDTA as sodium salts were special-grade reagents from Fluka and Akzo, respectively. The hydrotropes, such as TS, XS and CS, are Marchon (Italy) commercial products of ca. 93% purity, recorded using a Bruker WP 80 FT spectrometer operating at 20.13 MHz at ambient probe temperature (ca. 40 C) with broad-band proton decoupling. All chemical shift data, δ in ppm from external TMS reported in this study, were obtained from water solution ($\text{H}_2\text{O} + \text{D}_2\text{O}$) at a concentration of ca. 20% active agent. D_2O was always added at ca. a 5% concentration for internal lock purposes. The reference was a capillary of TMS in CCl_4 . The standard samples of Table 1 were used as is, dissolved in water.

TABLE 1
Surfactants and Related Compounds Investigated

Symbolic and compound name	Chemical structure
Anionic surfactant	
LAS, Linear alkylbenzene sulfonate	$R_1(R)CH(C_6H_4)SO_3Na$
AS, Alkylsulfate	$R_1(R)CHCH_2OSO_3Na$
AES, Alkylethoxysulfate	$R_1(R)CHCH_2(OCH_2CH_2)_nOSO_3Na$
SAS, Sodium alkane sulfonate	$R_1(R)CHSO_3Na$
AOS, α -Olefin sulfonate	$\left\{ \begin{array}{l} R \text{ CH}=\text{CH} (CH_2)_nSO_3Na \\ R \text{ CH}(\text{OH}) (CH_2)_nSO_3Na \end{array} \right.$
SP, Soap	$CH_3(CH_2)_nCOONa$
MES, Methylster α -sulfonate	$\left\{ \begin{array}{l} R \text{ CH}(\text{SO}_3Na)COOCH_3 \\ R \text{ CH}(\text{SO}_3Na)COONa \end{array} \right.$
Nonionic surfactant	
AE, Alkyl ethoxylate	$R_1(R)CHCH_2(OCH_2CH_2)_nOH$
CDE, Coco diethanolamide	$CH_3(CH_2)_nCON(CH_2CH_2OH)_2$
Cationic surfactant	
QUAT, Quaternary ammonium tetrasubstitute	$R_n(CH_3)_{4-n} N^+Cl^-$, $4 > n$
Hydrotrope	
TS, Toluene sulfonate	$CH_3(C_6H_4)SO_3Na$
XS, Xylene sulfonate	$(CH_3)_2(C_6H_3)SO_3Na$
CS, Cumene sulfonate	$(CH_3)_2CH(C_6H_4)SO_3Na$
UR, Urea	NH_2CONH_2
Chelant	
NTA, Nitrilotriacetic acid	$N(CH_2COOH)_3$
EDTA, Ethylenediaminetetraacetic acid	$(HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)_2$
Solvent	
Ethanol	CH_3CH_2OH
Methanol	CH_3OH
Glycols	$HO(CH_2)_{n>1}OH$
Germicidal agent	
Formaldehyde	$CH_2(OH)_2$
Inorganic constituent	
Carbonates	Na_2CO_3
Bicarbonates	$NaHCO_3$

Some commercial detergents, mainly the liquid ones, were analyzed by dissolving them in water, without any preliminary treatment. For other detergents the analyses were run on an ethanol extract.

The spectrometer experimental conditions usually were as follows: 16 K data points, 5000 Hz spectral width, 40° pulse width with NOE, time delay 3 sec, ca. 5,000 repetitive scans.

A suitable ^{13}C NMR spectrum of a commercial product or of its extract can be obtained in an average time of no more than three hr.

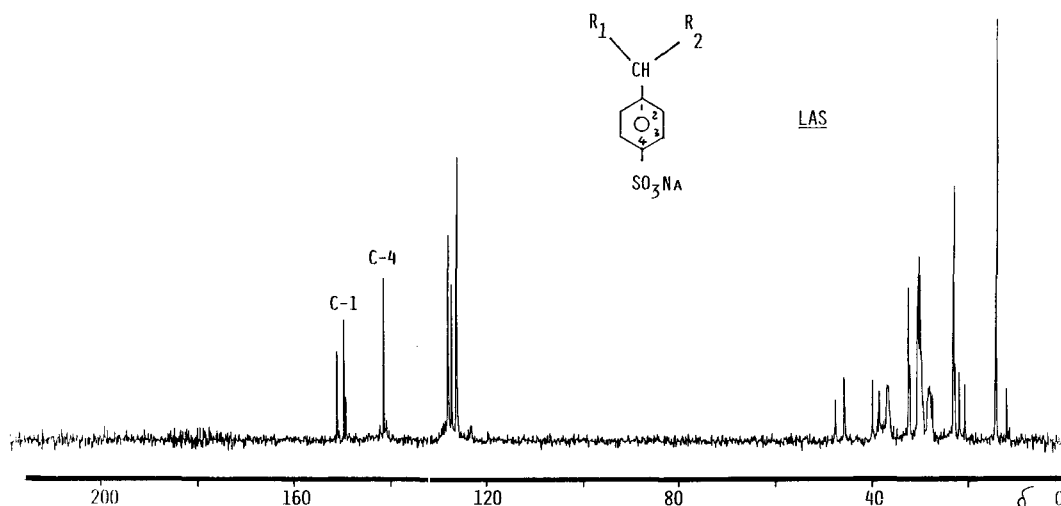
The active agent, when necessary, was obtained from the commercial detergent by means of ethanol extraction. Twenty-five g of detergent were treated with 500 ml of ethanol (95%) in a suitable flask connected to a reflux condenser. After boiling gently for ca. one hr, the slurry was filtered and the ethanol solution evapor-

ated under N_2 . The residue so obtained, dried to constant weight, was then dissolved in water for the NMR analysis. If necessary, dissolution of the extract in water can be aided with ethanol (1-2%).

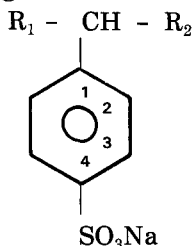
ANIONIC SURFACTANTS

Linear alkylbenzenes (LAS). The linear alkylbenzene sulfonates (LAS), as sodium salts, are the most widely used anionic surfactants in detergency. The corresponding parent linear alkylbenzenes (LAB), from which LAS's are obtained by sulfonation, are industrially produced by two routes:

- Benzene alkylation with n-olefins via HF
- Benzene alkylation with n-chloroparaffins via $AlCl_3$.

^{13}C NMR IDENTIFICATION OF SURFACTANTS IN MIXTUREFIG. 1. Typical ^{13}C NMR spectrum of LAS in water.

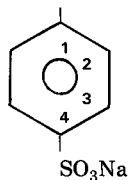
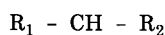
The LAS's have a general structure such as:



were the alkyl group is primarily a straight chain, usually in the C_{10} - C_{13} range. All possible isomers from the aromatic ring attachment of the carbons of an n-paraffin chain are present, with the exception of that of the terminal paraffin carbons, namely the 1-substituted paraffins. Figure 1 shows a typical ^{13}C NMR spectrum of LAS in D_2O .

The alkyl carbons are centered at $\delta = 10$ -50, whereas the aromatic carbons give two major resonance bands, those of the substituted carbons at $\delta = 140$ -152 and those of the unsubstituted carbons at $\delta = 125$ -130. A spectral ^{13}C NMR characteristic of LAS's useful for their identification is the resonance of the aromatic 4-carbon, bearing the SO_3Na substitution, which is constant at $\delta = 141.6$ for all homologs and isomers. Other diagnostic resonances of importance are the three bands of the substituted aromatic 1-carbon at high field, and the corresponding bands of the alkyl $>\text{CH}$ -carbon. The assignments are reported in Table 2. The most important resonances are those assigned to the 2-phenyl isomers, $\delta = 40.2$ and $\delta = 150.7$, for the $>\text{CH}$ -alkyl carbon and the aromatic 1-carbon, whose relative intensities make it possible to determine whether the parent LAB has been produced via HF or via AlCl_3 .

TABLE 2

 ^{13}C NMR Chemical Shifts of LAS's^a

Alkyl carbon	10 - 50
Substituted aromatic carbon	140 - 152
Unsubstituted aromatic carbon	125 - 130

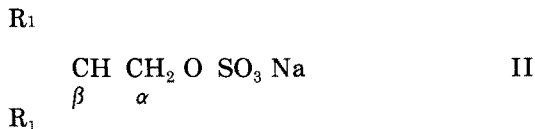
Isomer	1	2	3	4	(-CH<)	Intensity (%) ^b	
						Via HF	Via AlCl_3
2-Phenyl	150.7	127.1	126.2	141.6	40.2	18.4	30.6
3-Phenyl	149.0	127.6	126.2	141.6	48.2	21.3	18.7
4,5, . . Phenyl	149.3	127.6	126.2	141.6	46.1-46.4	60.3	50.7

^a δ Values from TMS.

^bRelative intensities are measured on the basis of peak integration of the alkyl-substituted aromatic carbons.

In fact, LAB's via HF have a 2-phenyl isomer content of ca. 18%, whereas those via AlCl_3 are near 30%.

Alkyl sulfate (AS). The alkylsulfates, e.g. sodium salts, derive from treating fatty alcohols, usually in the C_{10} - C_{15} carbon range, with SO_3 (but also with sulphuric acid or chlorosulphonic acid). The general formula is as follows:



where R is a linear alkyl chain and R_1 can be either hydrogen (linear alcohol derivatives) or methyl or ethyl, etc. (branched alcohol derivatives).

As known, the natural alcohols are exclusively of linear type, whereas the oxo-synthetic alcohols are usually of branched type with a linearity which ranges from ca. 40% to 80%, according to the different production processes.

Two major resonances are of importance for AS, one due to α - CH_2 's and the other due to the β -carbons. Those most useful for analytical purposes are those due to α - CH_2 's in the 70-76 δ range. Assignments of the various possible isomers are reported in Table 3. A typical ^{13}C NMR spectrum is shown in Figure 2. Considering the α - CH_2 pattern, only one signal at $\delta = 69.6$ is expected for the derivatives of the natural fatty alcohols. A complex pattern in the same spectral region, on the contrary, is displayed when AS's parent branched synthetic alcohols are involved. In the latter case the ratio of the various signals can be used to identify the type of parent alcohol and consequently to predict its production process.

Alkylethoxysulfate (AES). These derivatives, likewise the AS's, come from fatty alcohols of the C_{10} - C_{15} carbon range, which are first treated with ethylene oxide, then sulphated with SO_3 and eventually neutralized. They have a general formula such as:

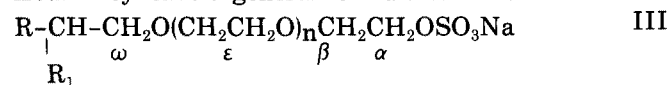


TABLE 3

 ^{13}C NMR Chemical Shifts of AS's^a

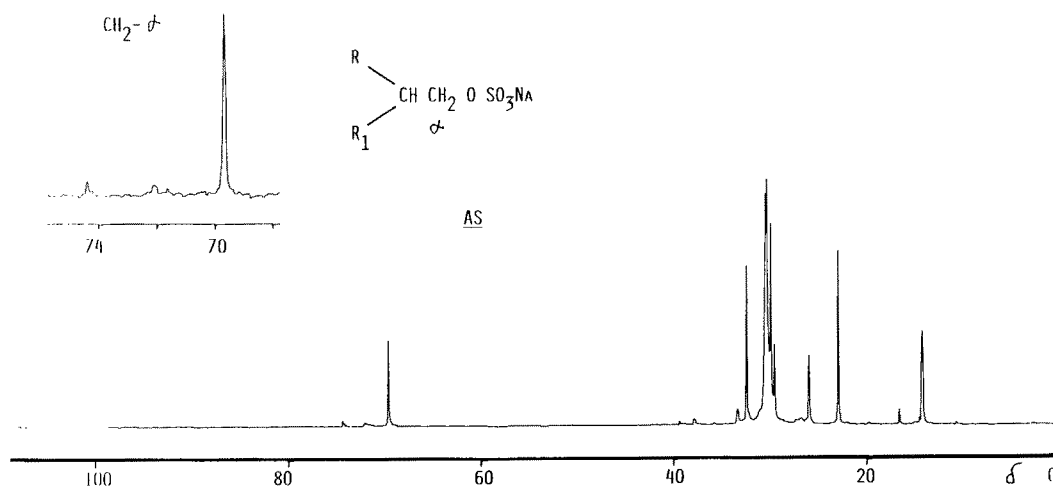
II	R_1	α	β
	H	69.6	33.2
	Me	74.4	35.8
	Et	71.6	39.3
	n-Pr	72.1	37.7
	n-Bu, etc.	72.1	37.9

^a δ Values from TMS.

R = linear alkyl chain.

where R and R_1 have the same meaning as for the AS's. The resonances of interest are those of the ω - CH_2 's and of the $>\text{CH}$ -carbons (with the ω - CH_2 's having a greater diagnostic value), which are sensitive to the R and R_1 groups, i.e., to the nature of the parent alcohol (linear or branched alcohol). The most intense signal in the ω - CH_2 region is at $\delta = 71.4$ due to the component coming from the linear parent alcohol. The resonances of the α - CH_2 and β - CH_2 groups are insensitive to the alkyl chain and are rather constant at $\delta = \text{ca. } 67$ and $\delta = \text{ca. } 69$, respectively. The β - CH_2 's, however, are often obscured or partially overlapped by the larger signal of the ϵ - CH_2 's.

The chemical shift assignments are reported in Table 4. A typical ^{13}C NMR spectrum is shown in Figure 3. Likewise, α - and β - CH_2 's, the ϵ - CH_2 groups, due to the ethylene oxide repetitive unit, give a single, rather broad signal centered at $\delta = \text{ca. } 70$. The relative intensity of this signal compared to those of α - and β - CH_2 carbons (mainly the α - CH_2 ones) can be used to evaluate the repetitive n value of the ethylene oxide unit.

FIG. 2. Typical ^{13}C NMR spectrum of AS in water.

^{13}C NMR IDENTIFICATION OF SURFACTANTS IN MIXTURE

TABLE 4

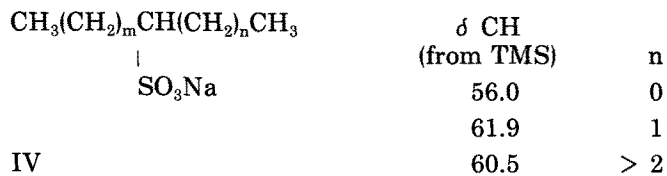
 ^{13}C NMR Chemical Shifts of AES's^a

III	R-CH-CH ₂ O(CH ₂ CH ₂ O) _n CH ₂ CH ₂ OSO ₃ Na				
		ω	ε	β	α
	R ₁				
	α carbon			67	
	β carbon			69	
	ε carbon			70	
	ω carbon			71-78	
	R ₁	ω			(>CH-)
	H	71.4			33.2
	Me	77.0			35.8
	Et	74.5			39.3
	n-Pr	74.7			37.3
	n. Bu, etc.	74.7			37.9

^aδ Values from TMS.

R = linear alkyl chain.

Sodium alkane sulfonate (SAS). Under this category of surfactants are included all those products which contain one or more SO₃X groups randomly linked to a secondary carbon along a linear paraffin chain (usually in the C₁₄-C₁₈ range). They can be obtained by chlorosulfonation or sulfoxidation of linear alkanes. For the monosulfonates the following general formula can be assigned:

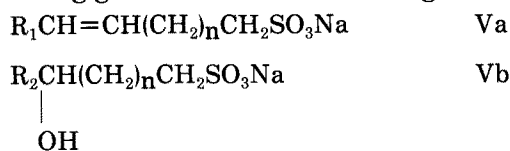


where m + n = 11-15.

The substituted secondary carbons resonate in the δ range of 55-63. Usually, only three bands are exhibited for water solutions.

The most intense band is that at δ = 60.5, due to the components with SO₃Na substitution in the most internal positions of the n-alkane chain. The relative intensities observed would tend to show a nearly statistically random substitution over all the secondary carbons of the n-alkane chain, in agreement with some HPLC evidences (unpublished results).

α-Olefin sulfonate (AOS). The sulfonation of the α-olefins, usually of the C₁₄-C₁₈ carbon range, give a complex crude mixture whose main components are sulfonic acids and sultones. After hydrolysis with excess of NaOH, one gets the sodium salts of the alkene sulfonic acids and of the hydroxyalkane sulfonic acids. The following general formulas can be assigned to them:



Three spectral regions are of major interest, as shown below:

Carbon structure	δ Range (values from TMS)
-CH ₂ SO ₃ Na	48-56
>CHOH	71
=CH-	119-140

This surfactant already has been studied by ^{13}C NMR, and several carbon assignments already have been reported (7). In Table 5 are listed the chemical shifts and the assignments of those components which are significantly abundant in the commercial products. Among the hydroxysulfonic derivatives, only the 3-hydroxy component (n=1) is normally present. This exhibits two characteristic signals at δ = 48.5 and δ = 70.7 for the -CH₂SO₃Na and the >CHOH carbons, respectively.

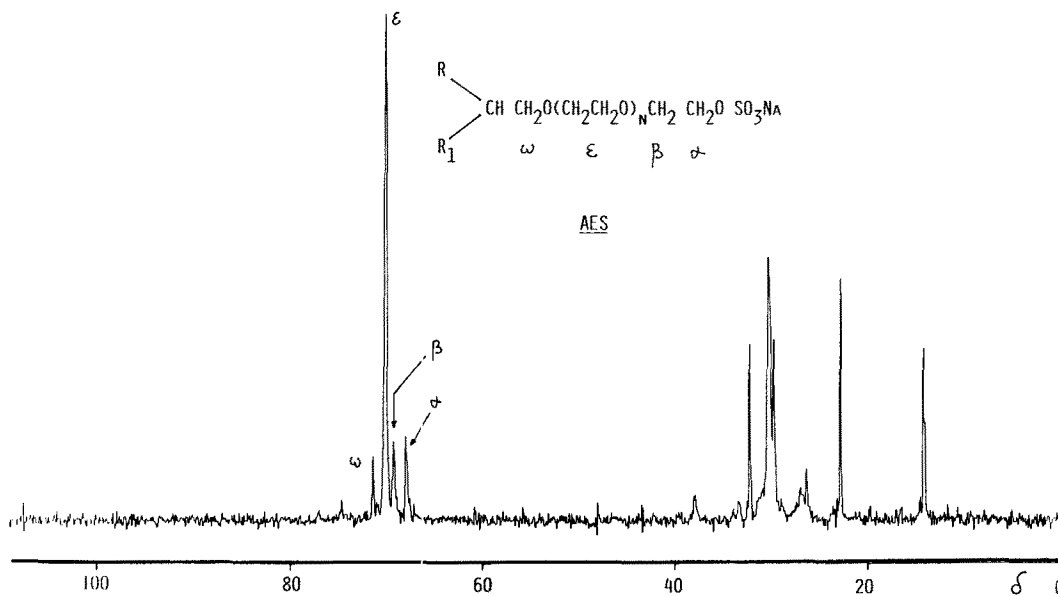
FIG. 3. Typical ^{13}C NMR spectrum of AES in water.

TABLE 5
 ^{13}C NMR Chemical Shifts of AOS's^a

Va		α	β	γ
$R_1\text{CH}=\text{CH}(\text{CH}_2)_n\text{CH}_2\text{SO}_3\text{Na}$	$\begin{matrix} \gamma & \beta & \alpha \end{matrix}$			
n				
0	2-alken-, isomer <i>trans</i>	55.3	119.9	138.7
0	2-alken-, isomer <i>cis</i>	50.3	119.5	136.5
1	3-alken-, isomer <i>trans</i>	51.7	127.6	132.3
1	3-alken-, isomer <i>cis</i>	51.5	127.4	131.8
> 1		51.7	130.7	130.7

Vb		α	β	
$R_2\text{CH}(\text{CH}_2)_n\text{CH}_2\text{SO}_3\text{Na}$	$\begin{matrix} \beta & \alpha \\ & \\ \text{OH} & \end{matrix}$			
3	3-hydroxy	48.5	70.7	—

^a δ Values from TMS.

In the case of alkenesulfonic derivatives, the most abundant component is usually the *trans* isomer of the 2-alkene derivative ($n=0$), of which the $-\text{CH}_2\text{SO}_3\text{Na}$ carbon strongly resonates at $\delta = 55.3$.

Soap, SP and methylester α -sulfonates, MES. These two other anionic surfactants, which were observed by us occasionally in some formulas, are worth being mentioned. The SP's are fatty acid salts (VI), whereas the MES's derive from treating fatty acid-methyl esters FAMES with SO_3 .

In the latter case, after neutralization with NaOH, two main components are produced: VIIa and VIIb. Both surfactants can easily be identified by ^{13}C NMR if present in the commercial detergents.

		1	2	3
VI	$\begin{matrix} 1 \\ \text{RCH}_2\text{COONa} \end{matrix}$	183.0	—	—
VIIa	$\begin{matrix} 2 & 1 & 3 \\ \text{R} - \text{CH} - \text{COOCH}_3 \\ \\ \text{SO}_3\text{Na} \end{matrix}$	170.4	66.2	53.1
VIIb	$\begin{matrix} 2 & 1 \\ \text{R} - \text{CH} - \text{COONa} \\ \\ \text{SO}_3\text{Na} \end{matrix}$	173.9	68.3	—

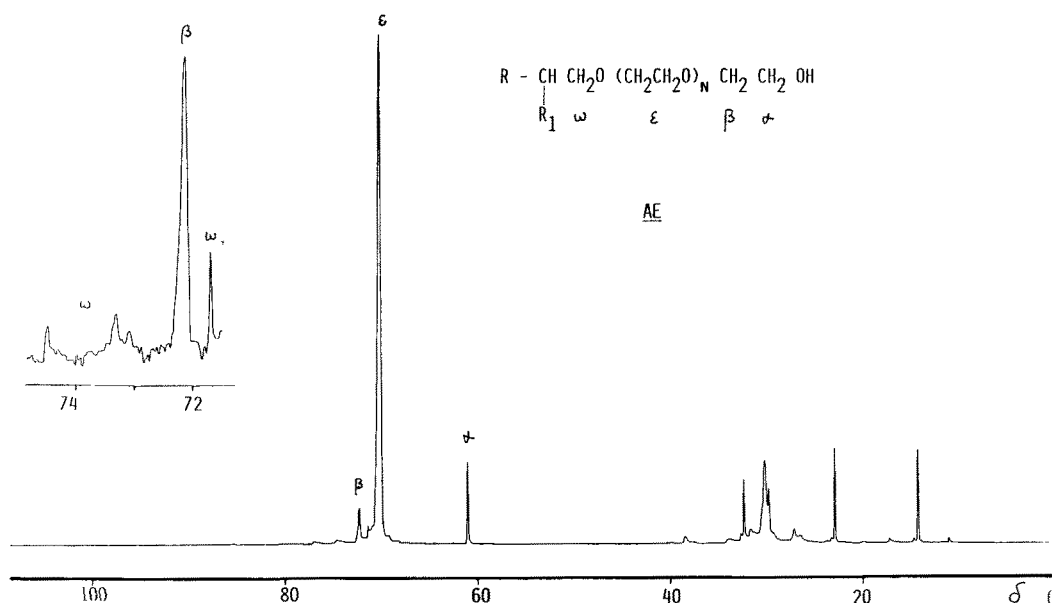


FIG. 4. Typical ^{13}C NMR spectrum of AES in water.

TABLE 6

¹³C NMR Chemical Shifts of AE's^a

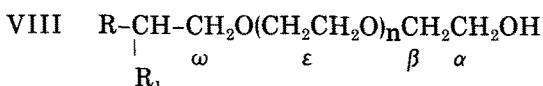
R-CH-CH ₂ O(CH ₂ CH ₂ O) _n CH ₂ CH ₂ OH		
R ₁	ω	ε β α
	α carbon	61.0
	β carbon	72.3
	ε carbon	70
	ω carbon	71-78
R ₁	ω	>CH-
H	71.4	33.2
Me	77.0	35.8
Et	74.5	39.3
n-Pr	74.7	37.3
n. Bu, etc.	74.7	37.9

^aδ Values from TMS.

Soaps can be identified by one resonance, that of the carboxyl group carbon which appears quite sharp at δ = 183.0 in a spectral region usually free from other signals. The identification of MES's, on the contrary, can be done with the help of a series of characteristic signals, usually five with chemical shifts as shown in VII.

NONIONIC SURFACTANTS

Alkylethoxylate (AE). Most of the nonionic derivatives present in the market are reaction products of ethylene oxide with fatty alcohols, usually of the C₁₀-C₁₅ carbon range. These derivatives are manufactured to contain a variable number of ethylene oxide groups, and each product contains a large number of telomers. These products may also contain some percent of free polyethylene oxide. The following general formula can be drawn:

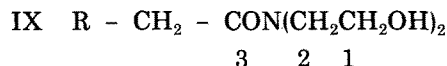


where R and R₁ have the same meaning as for the AS's and the AES's. Both α-CH₂ and β-CH₂ resonances are very characteristic and appear at δ = 61.0 and δ = 72.3, respectively, each as a single peak, insensitive to the structure of R and R₁ groups. These two signals are definite evidence for the presence of AE.

The resonances of the ω-CH₂ and CH- carbons are of interest if we want to get information on the nature of the parent alcohol. The assignments known are reported in Table 6 (8,9). A typical ¹³C NMR spectrum is shown in Figure 4. Only one signal is observed for ω-CH₂ carbon, δ = 71.4, when the natural alcohols or the predominantly synthetic linear alcohols are involved. Ethylene oxide repetitive units give a single band at δ = ca. 70. Again, relative intensities of ε-CH₂ with respect to α-CH₂ and/or β-CH₂ are useful for evaluating the length of the ethylene oxide repetitive units. Any

free polyethylene oxide present is evidenced by an additional sharp signal, which absorbs near that of the β-CH₂ at a slightly higher magnetic field, δ = ca. 72.

Coco diethanolamide (CDE). Other important non-ionic surfactants, which usually occur in dishwashing liquids shampoos and foam baths, are the fatty alkanol-amides, such as the coco diethanolamide, IX.



1 = centered at 60.6 δ

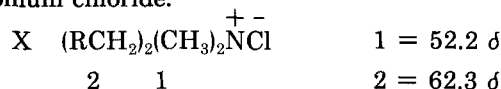
2 = centered at 50.0 δ

3 = 175.9 δ

This surfactant, one of the most representative of this category, has three diagnostic chemical shifts, as shown in IX. δ₁ and δ₂ are usually doublets, rather broad because of the N asymmetry and the hindered rotation around the C-N bond; their pattern and chemical shifts are dependent on concentration, pH and temperature.

CATIONIC SURFACTANTS

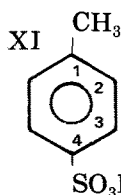
The long chain quaternary ammonium compounds (QUATS) are the most important class of commercial cationic surfactants. They can easily be identified by their ¹³C NMR spectrum, which can also give some useful structural information. As an example, in X we report only the resonances of CH₂ and CH₃ linked to nitrogen for the dimethyl-dihydrogenated tallow ammonium chloride.



Different signals for CH₃ and CH₂ bonded to nitrogen are obtained in the same spectral region for the mono-, di- and tri-methyl derivatives, which allow one to obtain either qualitative or quantitative data, as already reported in the literature (10).

HYDROTROPES

Toluene sulfonate (TS). The commercial product is a mixture of the para- and ortho-disubstituted benzene derivatives, where the para-derivative is usually the most abundant one.



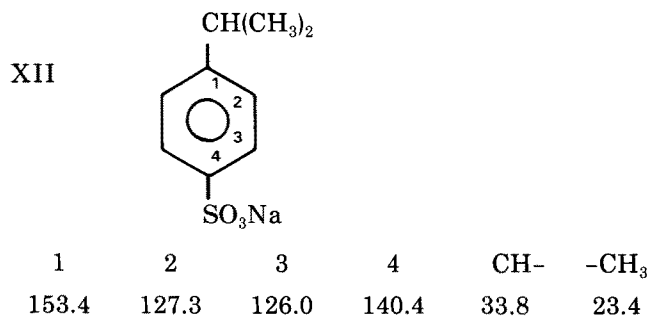
1	2	3	4
146.9	129.8	125.8	140.0

The substituted carbons are in the range δ = 135-147, whereas the unsubstituted ones are at δ = 125-130. For the para-derivative, as shown in XI, the two signals of 2 and 3 are twice the intensity of 1 and 4. The methyl carbon resonates at δ = 20.9 for the para-derivative and at δ = 20.1 for the ortho.

Xylene sulfonate (XS). The commercial product is a complex mixture of isomers which give a complicated

spectrum. The aromatic carbons give a series of peaks (more than 15) in the δ range of 122–150, and the methyl carbons (7–8 peaks) resonate at $\delta = 14$ –30. A complete assignment is not known as far as we know. However, the ^{13}C NMR spectrum pattern is quite characteristic, and it can be easily used as a “fingerprint” to identify the presence of this specific hydrotrope.

Cumene sulfonate (CS). The commercial product usually contains only the paraisomer, as shown in XII:



Signals for the unsubstituted aromatic carbons, 2 and 3, are twice as intense as for the substituted ones, 1 and 4.

Urea (UR). One signal at $\delta = 163.0$.

Others. Other useful ^{13}C NMR resonances, due to some chelants, solvents, germicidal agents and inorganic constituents frequently encountered in the commercial formulations, are summarized in Table 7. EDTA gives three signals with relative intensities 2:2:1.

Analysis of commercial products. Several commercial household detergents and shampoos have been analyzed in our laboratories using the ^{13}C NMR technique and the spectral information just reviewed. The results were always obtained from a single spectrum of a concentrated water solution (ca. 20%), using the commercial product “as is” when possible, or its corresponding ethanol extract. The spectrum accumulation requires no longer than three hours. In Figures 5 and 6 two examples of ^{13}C NMR spectra of commercial detergents

TABLE 7

Useful Resonances of Practical Interest in the Analysis of Formulates by ^{13}C NMR Technique^a

		1	2	3
NTA	$\text{N}(\text{CH}_2\text{COO}^-)_3\text{Na}_3^+$ 2 1	179.8	59.3	—
EDTA	$-\text{CH}_2\text{N}(\text{CH}_2\text{COO}^-)_2\text{Na}_2^+$ 3 2 1	171.1	58.4	52.0
	$\text{CH}_3\text{CH}_2\text{OH}$	17.6	57.7	—
	CH_3OH	49.3	—	—
	$\text{HOCH}_2\text{CH}_2\text{OH}$	63.5	—	—
	HOCH_2OH	82.3	—	—
	CO_3^{2-}	161	—	—
	HCO_3^-	168	—	—

^aValues from TMS.

present in the market are shown. Sample A is an ethanol extract from a typical powder household detergent, and sample B is a typical dishwashing liquid. From an inspection of the ^{13}C NMR spectra one can easily get the following information. Sample A is made up mainly of LAS, AE and AS as surfactants, in the relative ratio of 2:1:1, respectively. The “parent” linear alkylbenzene (LAB) is a via-HF product, and the alcohol of the AE and AES derivatives is of synthetic nature with ca. 60% branching. The ethylene oxide content is ca. 12 moles with respect to the alcohol. Sample B contains mainly LAS and AES, as surfactants, in the relative ratio of 4:1, respectively. In this case the LAB “parent” is a via AlCl_3 product and the alcohol of the AES derivative is predominantly of linear nature. The ethylene oxide content is ca. three moles with respect to the alcohol.

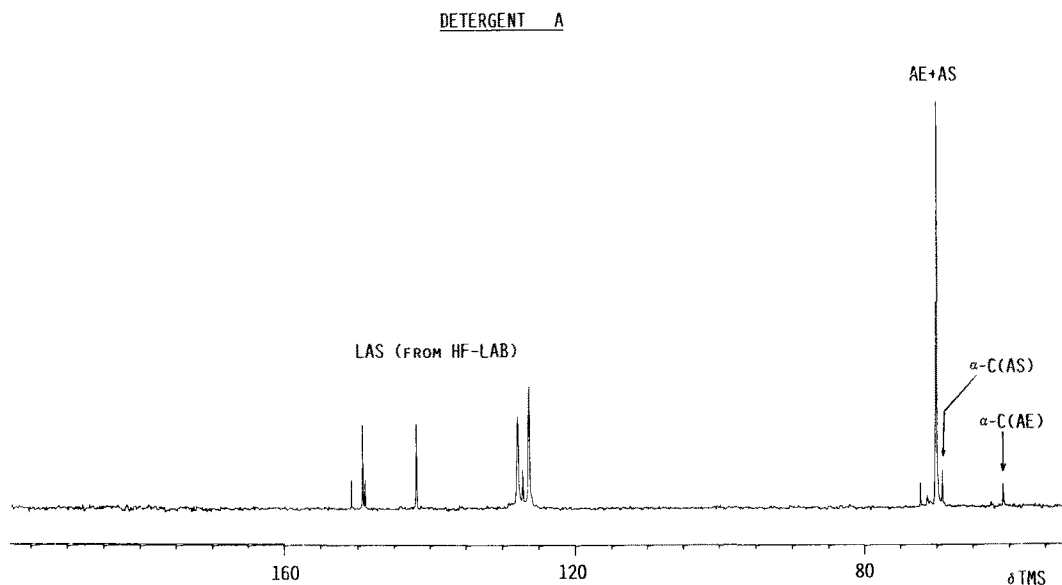


FIG. 5. ^{13}C NMR spectrum of an ethanol extract of a typical powder household detergent (sample A).

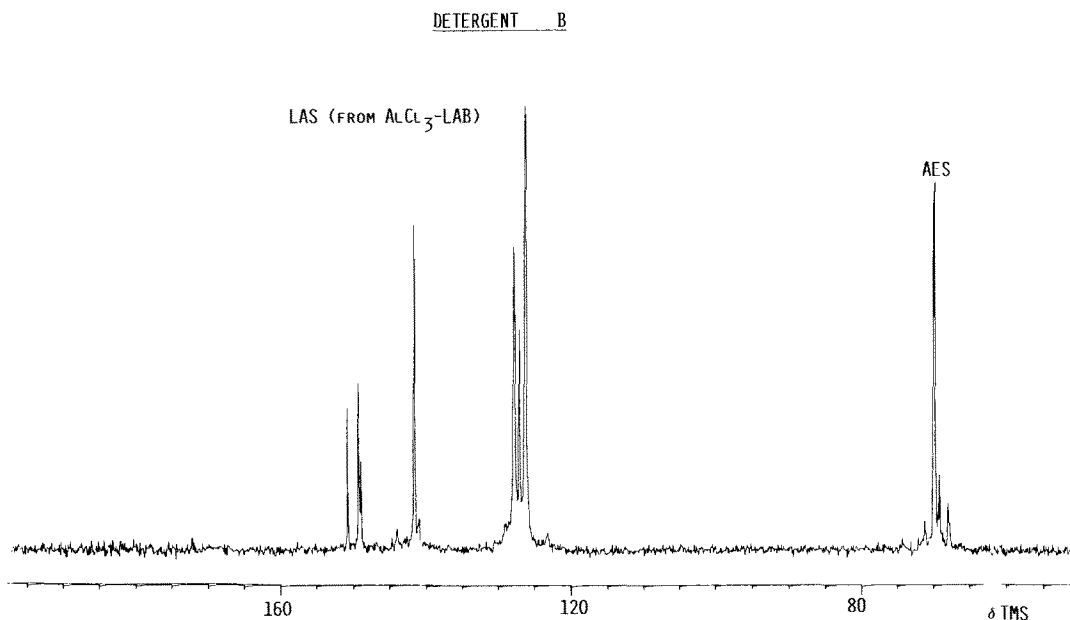
^{13}C NMR IDENTIFICATION OF SURFACTANTS IN MIXTURE

FIG. 6. ^{13}C NMR spectrum of a typical dishwashing liquid as is (sample B).

In general, the following information can be gained by this kind of analytical approach:

- Determination of the type of surfactants, even if present in mixtures.
- For LAS derivatives, evaluation of the relative ratio of isomers and identification of the corresponding "parent" LAB, i.e. via-HF or AlCl_3 .
- For the alcohol derivatives, evaluation of the alcohol linearity, i.e. natural or synthetic alcohol.
- For the ethylene oxide derivatives, evaluation of the average length of the ethoxy repeating unit.
- Semiquantitative results on relative concentrations of the various surfactants.
- Identification of several nonsurfactant components such as hydrotropes, silicones, chelants, germicidal agents and inorganic constituents.

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