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The Use of High Resolution NMR Spectroscopy for Characterizing Petroleum Sulfonates

by

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ABSTRACT

Natural petroleum sulfonates and synthetic sulfonates were characterized or "finger-printed" using high resolution NMR spectroscopy. Natural petroleum sulfonates are produced by sulfonation of a selected petroleum fraction. Synthetic sulfonates are produced by sulfonation of alkylated benzenes or naphthalenes of the proper equivalent weights. Petroleum sulfonates usually contain unreacted oil, water, and salts in addition to the active petroleum sulfonate. Therefore, the qualtiy and composition of similar petroleum sulfonates may be different if one considers the supply of a petroleum sulfonate at different time intervals or pooling of similar petroleum sulfonates obtained from different suppliers. Characterization of petroleum sulfonates generally includes (1) the average equivalent weight, (2) percentage of unreacted oil, water, and salts, (3) percentage of active sulfonate, (4) pH and solubility of oil or water. A rapid and informative analysis or "finger-printing" of petroleum sulfonates can be done using high resolution NMR spectroscopy. The relative amount of water, the relative amounts of aromatic and aliphatic protons, the fine structure of the polar group and hydrocarbon chains can be determined by this method.

References and illustrations at end of paper

About 20 different types of petroleum sulfonates were analyzed using high resolution NMR spectroscopy.

INTRODUCTION

Petroleum sulfonates are widely used as surface active agents in the injection fluid (detergent solution) to lower the interfacial tension between oil and formation water in the tertiary oil recovery process. It was found that a low interfacial tension (LIFT) in the order of 10^{-2} dynes/cm or less is necessary for the injection fluid to displace the trapped oil after water flooding.[1] Further, it was found that the LIFT can be achieved only if the contacting oil phase is compatible with a given injection fluid.[2] This obviously leads to the suggestion that the molecular structure of petroleum sulfonates is vital to the achievement of LIFT for a given oil.

Natural petroleum sulfonates are generally mixtures of alkyl-aryl sulfonates which also contain unreacted oil, water and electrolytes. It is difficult to identify the individual components in the natural petroleum sulfonates unless each of them is separated. However, a rapid and informative analysis or "finger-printing" of petroleum sulfonates is highly desirable. The characterization of a petroleum sulfonate is a necessary task if

one considers the supply of a petroleum sulfonate at different time intervals or pooling of similar petroleum sulfonates obtained from different suppliers for field application.

High resolution nuclear magnetic resonance spectroscopy was used to characterize or "finger-print" various petroleum sulfonates. Among the information that can be deduced from high resolution NMR spectroscopy are: (1) the relative amount of water present in the sample, (2) the relative amounts of aromatic to aliphatic protons and (3) the fine structure of the polar group and hydrocarbon chains.

MATERIALS AND METHODS

Carbon tetrachloride (99% pure) was purchased from Chemical Sample Company. Chloroform (analytical grade) was purchased from Fisher Scientific Company. Deuterated water (99.8%) and Deuterated Chloroform (99.5%) were purchased from SIC (Stohler Isotope Chemicals). Water was double distilled.

Butyl benzene sulfonate and sodium dodecyl benzene sulfonate (SDBS, 85% active) were purchased from Pfaltz and Bauer Company. SDBS was purified by extraction with hot isopropyl alcohol and the extracts were dried by evaporation of isopropyl alcohol.

Steol KS 460, sodium-xylene sulfonate, pentadecyl-benzene sulfonate (PDBS), Petrostep 420, Petrostep 450 and Petrostep 465 were obtained from Stepan Chemical Company. PDBS and Petrostep 420 were dissolved in 40% aqueous isopropyl alcohol solution and extracted with hexanes. The hexane extract was discarded and remaining solution was dried to obtain the purified PDBS and Petrostep 420. Petroleum sulfonates TRS 10-18, 10-80, 10-410, 10-B, 10-40 and 10 were obtained from Witco Company. Synthetic sulfonates FA 400 and MECA 120 XS were obtained from Exxon Production and Research Company.

Petroleum sulfonate solutions were made homogeneous and stable by dissolving in proper solvents at a concentration of 10 to 20% (w/v).

High resolution NMR spectra of petroleum sulfonate solutions were taken by using JEOL 60 megacycle NMR spectrometer at 32°C. Tetramethylsilane (TMS) was used as an internal standard for chemical shift measurements.

RESULTS AND DISCUSSION

One class of petroleum sulfonates, which is generally called "natural petroleum sulfonates" or "Mahogany sulfonate", is the by-product of the manufacturing of white oil from sulfuric acid treatment of selected petroleum fractions.

The Mahogany petroleum sulfonates have a wide range of molecular weight, from 300 to 600, and different amounts of unreacted oil and water. Depending on the choice of petroleum fractions and sulfonation process, petroleum sulfonates of different qualities can be produced with varying degrees of surface activity and other physical properties that can be important in the formulation of surfactant solutions for enhanced oil recovery.

Another class of petroleum sulfonates is produced by sulfonation of alkylated benzene or naphthalenes of the proper equivalent weights. Sodium alkyl ortho-xylene sulfonate is a typical example. These are catagorized as synthetic petroleum sulfonates. A third class of petroleum sulfonates is produced by direct sulfonation of selected petroleum fractions using SO_3 gas.

In addition to the above three catagories, there are many other products of petroleum sulfonates developed by various companies for specific applications.

Consider the supply of a petroleum sulfonate at different time intervals by a manufacturer, or pooling of a similar petroleum sulfonate obtained from different suppliers; the question that can be raised is how one can be sure that a given surfactant is identical to the previous batch of the same sulfonate.

High resolution proton nuclear magnetic resonance spectroscopy has been used extensively as an analytical tool to determine the molecular structure of organic molecules which are mainly composed of carbon and hydrogen atoms.

In this study, high resolution NMR spectroscopy was used to solve some of the problems mentioned above. The relative amounts of aromatic to aliphatic protons, the relative amounts of water in a surfactant and the polar group structure of surfactant molecules were determined by this method.

The position of the resonance peaks in the PMR spectra, which has been called "chemical shift," represents the chemical environment of the protons observed. Chemical shift is caused by the shielding effect of electrons which move around the nuclei. The chemical shift has the symbol σ (or $\tau = 10 - \sigma$) and units of parts per million (PPM). In 60 mega cycle PMR, 1 PPM is equal to 60 cycle per second. The standard (or reference) most often being used to determine the chemical shift

is tetramethylsilane (TMS) which has been assigned a σ value equal to zero. All the other protons will resonate at lower magnetic fields than TMS: in other words, will have a higher chemical shift.

Chemical shift may be influenced by the electron negativity of the adjacent atoms. The higher the electron negativity of the adjacent atom, the greater is the chemical shift of the proton. For example, the proton in -OH of alcohol will shift to lower field than $-CH_3$ group. The aromatic protons will resonate at substantially lower fields than aliphatic protons due to the electron movement in the ring structure. Substitution of methyl protons with other groups will increase the chemical shift. For example, $R-CH_3$ has $\sigma = 0.9$ PPM, $R-CH_3$ has $\sigma = 1.2$ PPM and R-CH has $\sigma = 1.5$ PPM.

The protons located directly above or below the ring resonate at high field than the protons located on the same plane of the benzene ring. This is called "diamagnetic anisotropy effect" which results from the movement of the delocalized electrons. Those protons associated with a double bond, triple bond or ring structure will have this effect.

The area under a resonance peak represents the relative number of protons yielding the resonance peak. Since petroleum sulfonates are multicomponent mixtures of organic molecules, it is very difficult to identify the molecular structure just using a single spectrum. However, we can obtain some information or "fingerprinting" of a petroleum sulfonate from its PMR spectrum. The type of information that can be obtained from PMR spectra is summarized as follows:

(1) <u>The relative amount of aromatic to aliphatic protons</u>

Since aromatic protons have higher chemical shifts than aliphatic protons, their resonance peaks are separated and easy to identify. The ratio of aromatic to aliphatic protons is the ratio of their integrated resonance peak areas. The ratios of aromatic to aliphatic protons of various sulfonates are listed in Table 1.

The sulfonates with the higher equivalent weight have more aliphatic protons than the lower equivalent weight. For example, butylbenzene sulfonate with average aliphatic chain length of four carbons has 68.7 aromatic protons for 100 aliphatic protons, whereas in dodecyl-benzene sulfonates, with an aliphatic chain length of twelve, this value drops to 12.9 for 100 aliphatic protons. This can be seen also in the Witco series and Petrostep series petroleum sulfonates.

(2) <u>The relative amount of water in sulfonates</u>

The amount of water (% of total protons in the sample)in Petrostep sulfonates and Witco sulfonates TRS 10-40, TRS 10-B was higher than that in TRS 18, TRS 10-80 and TRS 10-410. This was estimated from the area under the water resonance peak. In TRS 10-410 and TRS 10-B, we have to use polar solvents such as 1% NaCl or $CDCl_3$ to dissolve them. The solubility of petroleum sulfonates in various solvents not only depends on their equivalent weight, but also depends on the amount of water or unreacted oil in the sample. Most of the petroleum sulfonates with equivalent weight range from 420 to 550 can be easily dissolved in CCl_4, which indicates that these sulfonates are oil soluble.

Individual spectra of petroleum sulfonates are shown in Figure 1 to Figure 20.

Figure 1 is the spectrum of sodium xylene sulfonate made by Stepan Chemical Company. Peaks at 1 PPM and 1.5 PPM are the two non-equivalent methyl protons. Peaks at 5.8 and 6.8 PPM are the non-equivalent aromatic protons. Pure xylene (ortho, para or meta isomers) give a single methyl proton peak and a single aromatic proton peak. The sodium xylene sulfonate gives rather complicated peaks for the aromatic region.

Figure 2 is the spectrum of butyl-benzene sulfonate made by Pfaltz and Bauer Company. The peaks located near 8 PPM are aromatic protons. Unlike the linear dodecyl benzene (a hydrocarbon oil) which has only one peak of aromatic protons, butyl-benzene sulfonates show a more complicated aromatic proton spectrum. The peaks from 0 to 2 PPM are aliphatic proton portions of the molecule.

Figure 3 is the spectrum of sodium dodecyl benzene sulfonate (SDBS) from Pfaltz and Bauer Company, which has 85% active SDBS and 15% salt as impurity. This compound cannot be dissolved in CCl_4 but can be dissolved in more polar solvents, such as $CHCl_3$. This is due to a large amount of salt impurities. Figure 4 is the purified SDBS without salt which can be dissolved in CCl_4. Aromatic to aliphatic proton ratio does not change after purification. However, the resonance peaks of the polar group are broader in CCl_4 than in $CHCl_3$.

Figures 5, 6 and 7 are spectra of Petrostep 465, 450 and 420, which were supplied by Stepan Chemical Company. These are so-called gas oil sulfonates which can be dissolved in CCl_4. The amount of water of these sulfonates is around 20% by weight, which is indicated by a large peak of water

protons. The relative amount of aromatic to aliphatic protons increases as the equivalent weight decreases, since higher equivalent weight sulfonate has longer alkyl chain length. Figure 8 is the spectrum of purified Petrostep 420, which does not have either unreacted oil or water. The water peak disappears in Figure 8. The portion of aromatic protons is increased. This shows that the unreacted oil molecules have more aliphatic protons than sulfonated oil.

Figures 9 to 15 are the spectra of Witco TRS series Mahogany sulfonates which are characterized by their mahogany color. Again, as the equivalent weight increases, the aromatic/aliphatic ratio decreases. They have less water content than Petrostep sulfonates. Solubility in oil decreases as the equivalent weight decreases. TRS 18 (EW 508), TRS 10-80 (EW 420) and TRS 10-410 (EW 418) are fairly soluble in CCl_4. TRS 10-B (EW 396) requires more polar solvents such as $CDCl_3$ to dissolve it. TRS 10-40 (EW 338) only dissolves in aqueous solvents. Peaks of aromatic portions of TRS-18 and TRS 10-80 were enlarged by increasing the signal gain and are shown in Figure 9 and 10 right above the original spectra. Two peaks are detected which come from the non-equivalent aromatic protons.

Figure 16 is the spectrum of KS 460, a sodium alkyl ether sulfate made by Stepan Chemical Company.

(3) The structure of polar and nonpolar parts of a surfactant

Figure 17 is the spectrum of a synthetic sulfonate from Stepan Chemical Company with equivalent weight corresponding to pentadecyl benzene sulfonate (PDBS). The aromatic portion is rather significantly different compared to either Petrostep sulfonates or Witco series sulfonates. Figure 18 shows the spectrum of de-oiled PDBS. The aromatic portion is not significantly changed after the de-oiling procedure.

Figures 19 and 20 are the spectra of synthetic ortho-xylene sulfonates FA 400 and MECA 120 XS which have been used by Reed and coworkers at Exxon Production Research Company. The aromatic portions of these sulfonates are significantly higher than those of the mahogany sulfonates or gas-oil sulfonates. The spectra of the aliphatic portion are more complicated than those of the other petroleum sulfonates.

Crutchfield et. al.[3] have applied a 60 megacycle high resolution NMR spectrometer to characterize detergent chemicals such as alkylbenzene, alkylphenols and ethyleneoxide adducts of alkylphenols. These chemicals can be used to produce detergents by chemical reactions to attach a polar group to them. Average lengths of alkyl chains, average molecular weights, degree and kind of branching in the alkyl chain, ortho-para distribution or aryl substituents and average lengths of EO chains were determined by this method.

In summary, it appears that the high resolution PMR spectra can serve as a "fingerprint" of petroleum sulfonates and can provide information about the aromatic/aliphatic proton ratio, percent water content of the sample and the structure of the polar and hydrocarbon chains of surfactant molecules.

APPLICATIONS

The information obtained by using high resolution NMR spectroscopy, including the water content of the sulfonates, the relative amounts of aromatic to aliphatic protons, and the fine structure of polar and hydrocarbon chains can be used to characterize or "fingerprint" various petroleum sulfonates. The method of using high resolution nuclear magnetic resonance spectroscopy to characterize petroleum sulfonates is rapid, quantitative and informative. Some of the structural differences of petroleum sulfonates revealed by this technique cannot be easily elucidated by other techniques. The NMR method also can be used to determine solubility of various alcohols in brine.

CONCLUSIONS

(1) High resolution NMR spectroscopy can be used to "finger-print" a petroleum sulfonate.

(2) For a series of similar petroleum sulfonates, such as Witco TRS series or Stepan Petrostep series, the relative amounts of aromatic to aliphatic protons decreases as the equivalent weight of petroleum sulfonate increases.

(3) The relative amounts of aromatic to aliphatic protons is also different for petroleum sulfonates obtained from different manufacturers. In general, this number is greater for the synthetic sulfonates than the natural petroleum sulfonates with the same equivalent weight.

(4) The relative amount of water determined by NMR spectroscopy, (in % of total protons), is surprisingly close to the water content on weight basis for most petroleum sulfonates.

(5) The high resolution NMR spectra of surfactants FA 400 and MECA 120 XS show fine structure of their polar group and hydrocarbon chain compared to natural petroleum sulfonates.

ACKNOWLEDGEMENTS

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3. Crutchfield, M.M., Irani, R.R. and Yoder, J.T.: "Quantitative Applications of High Resolution Proton Magnetic Resonance Measurements in the Characterization of Detergent Chemicals," J. Amer. Oil Chemists' Soc., 41, 129-132, 1964.

TABLE I

Sulfonates (Company)	[eq.wt.]	Solvent	Concentration (w/v)	NMR Data Water Content	Supplier's Data Water Content	Supplier's Data % Active	Aromatic/Aliphatic	Comments
Butyl-Benzene Sulfonate (Pfaltz and Bauer)	[213]	as in sample	as in sample	———	———	———	68.7%	
Sodium Dodecyl Benzene Sulfonate (Pfaltz and Bauer)	[348]	$CHCl_3$	3.5%	trace	trace	85	12.9%	(1) 15% salt impurity (2) not soluble in CCl_4
Sodium Dodecyl Benzene Sulfonate (Pfaltz and Bauer)	[348]	CCl_4	10%	trace	trace	100	12.9%	de-salted
Steol KS-460 (Stepan)		H_2O	10%	———	———	———	———	polyoxylated sulfate
Sodium-xylene Sulfonate (Stepan)		H_2O	20%	———	———	———	———	
Pentadecyl-Benzene Sulfonate (Stepan)	[390]	D_2O	12.5%	———	———	64	12.8%	as supplied
Pentadecyl-Benzene Sulfonate (Stepan)	[390]	$CDCl_3$	20%	trace	trace	∿ 100	14.2%	de-oiled and de-salted
FA 400 (ESSO Res. Engr)	[420]	CCl_4	20%	trace	trace	80^+	16.4%	synthetic xylene sulfonates
MECA 120XS (Exxon)	[420]	CCl_4	20%	trace	trace	86.5	17.95%	synthetic xylene sulfonates
TRS Series (Witco) TRS-18	[508]	CCl_4	20%	3.80%	5%	61	0.6%	
TRS-10-80	[420]	CCl_4	20%	7.69%	8.7%	79.8	2.4%	
TRS-10-410	[418]	CCl_4	25%	———	4.9%	61.8	3.5%	
TRS-10-B	[396]	$CDCl_3$	20%	20.9%	19%	61.3	7.2%	Mahogany Sulfonates
TRS-10-40	[338]	1% NaCl	25%	———	37%	41.6	14.1%	
TRS-10	———	CCl_4	20%	4.67%	———	———	2.5%	
Petrostep series (Stepan) 420	[420]	CCl_4	20%	19.5%	17.5%	60	6.1%	Gas-oil Sulfonates
420	[420]	CCl_4	20%	∿0	∿0	∿100	7.9%	de-oiled, de-salted, de-watered 420
450	[450]	CCl_4	20%	36.2%	24.5%	60	5.7%	
560	[560]	CCl_4	20%	26.2%	23.5%	60	5.0%	

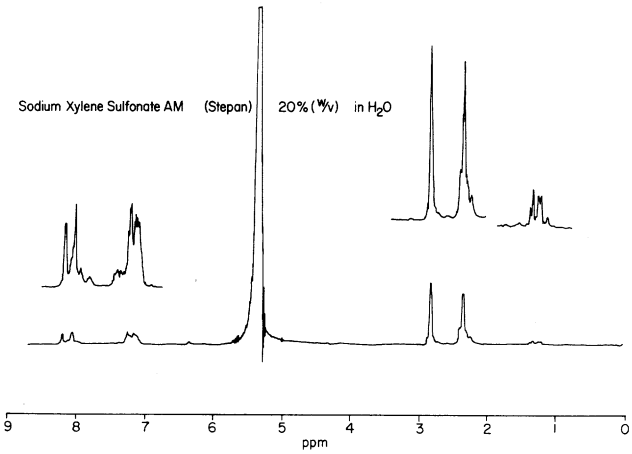

Fig. 1 - NMR spectrum of sodium xylene sulfonate AM.

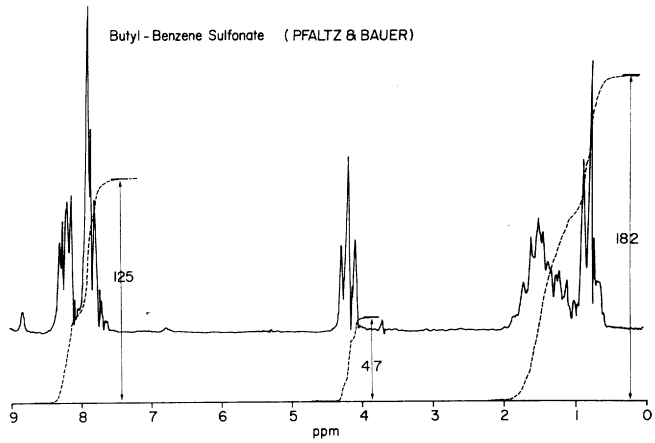

Fig. 2 - NMR spectrum of butyl-benzene sulfonate.

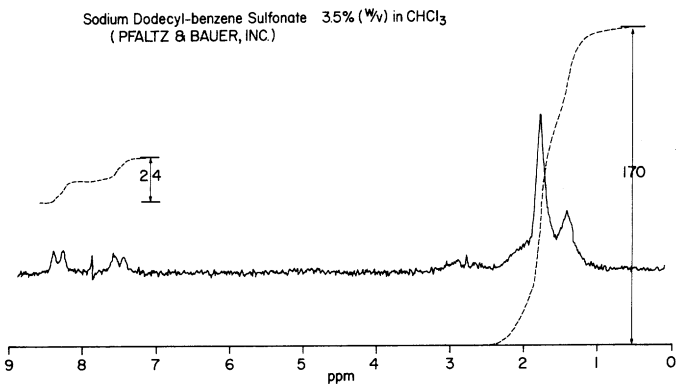

Fig. 3 - NMR spectrum of sodium dodecyl-benzene sulfonate.

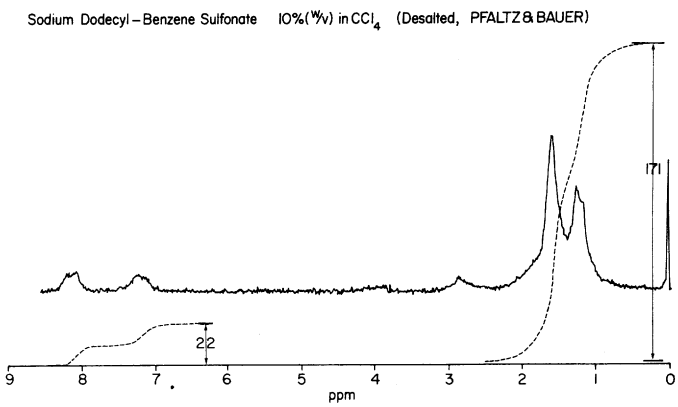

Fig. 4 - NMR spectrum of sodium dodecyl-benzene sulfonate (desalted).

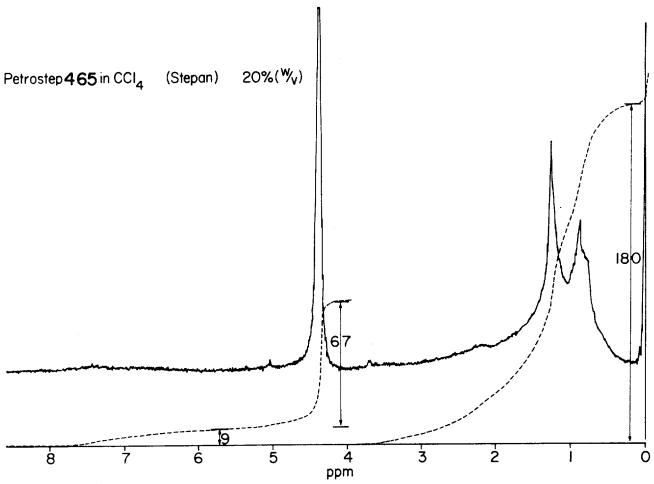

Fig. 5 - NMR spectrum of Petrostep 465 in CCl_4.

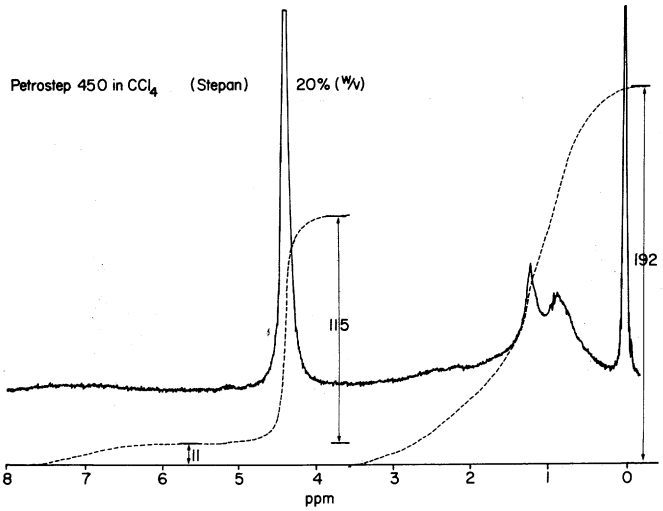

Fig. 6 - NMR spectrum of Petrostep 450 in CCl_4.

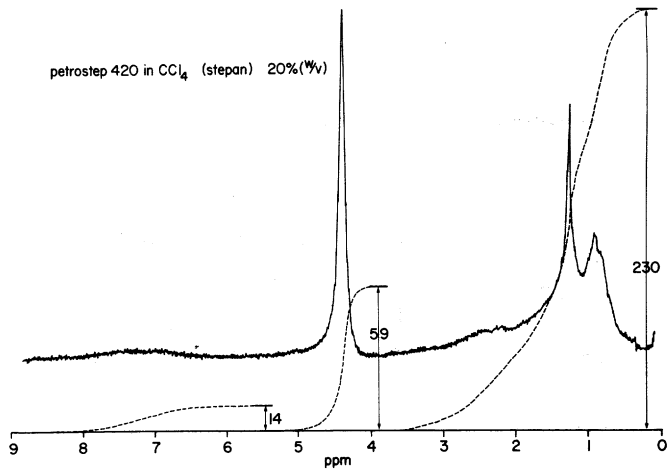

Fig. 7 - NMR spectrum of Petrostep 420 in CCl_4.

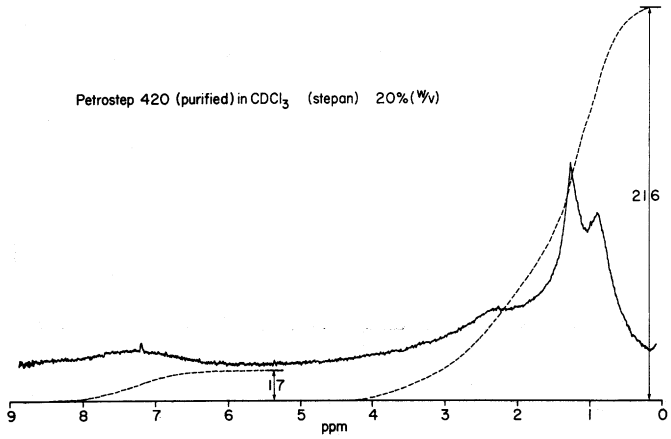

Fig. 8 - NMR spectrum of Petrostep 420 (purified) in $CDCl_3$.

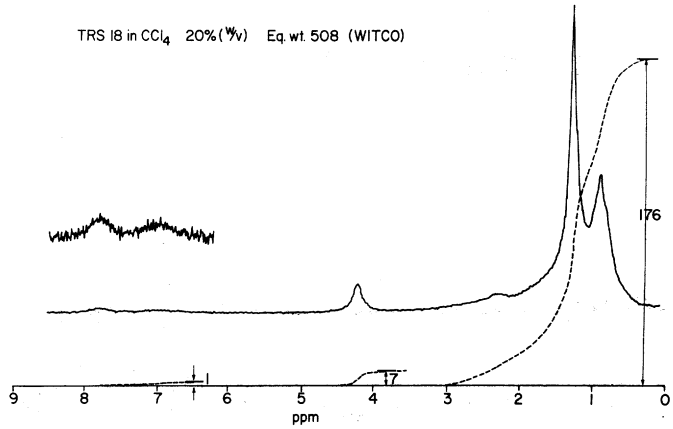

Fig. 9 - NMR spectrum of TRS 18 in CCl_4.

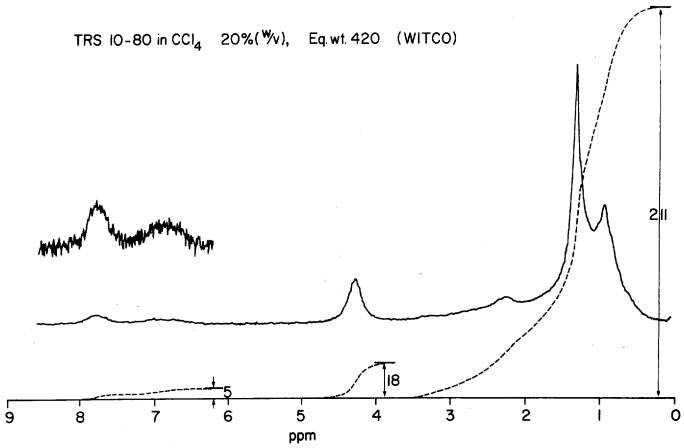

Fig. 10 - NMR spectrum of TRS 10-80 in CCl_4.

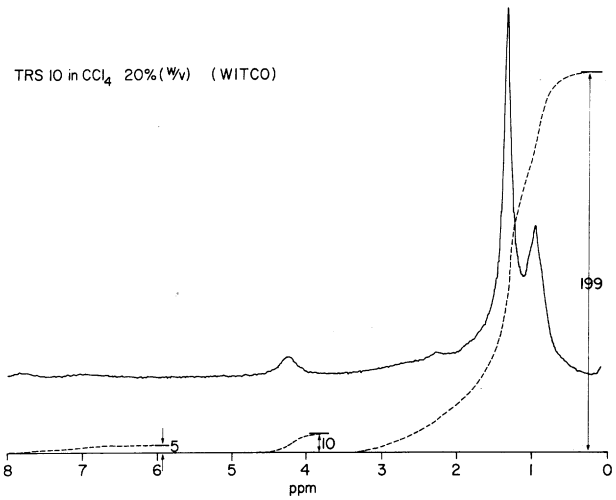

Fig. 11 - NMR spectrum of TRS-10-410 in CCl_4.

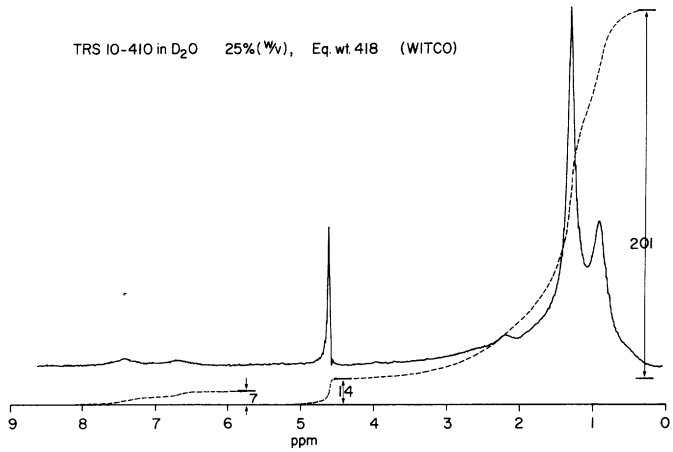

Fig. 12 - NMR spectrum of TRS 10-410 in D_2.

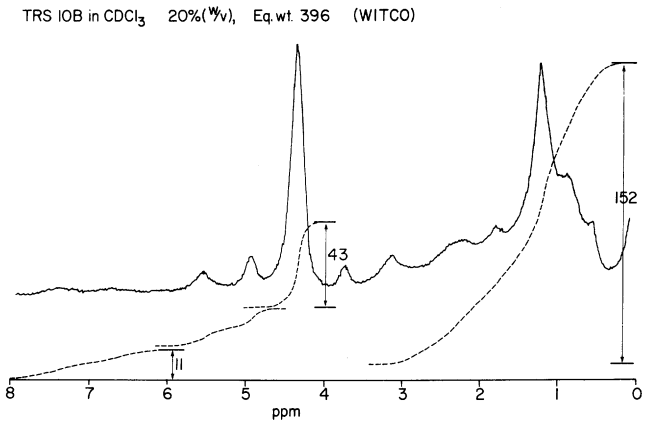

Fig. 13 - NMR spectrum of TRS 10B in $CDCl_3$.

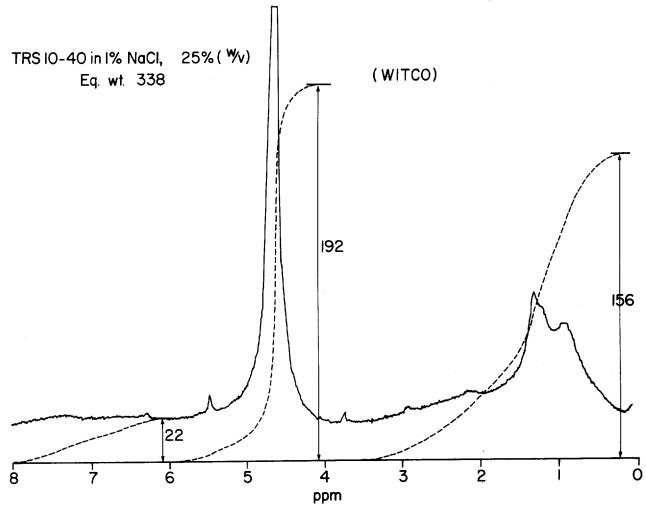

Fig. 14 - NMR spectrum of TRS 10-40 in 1% NaCl.

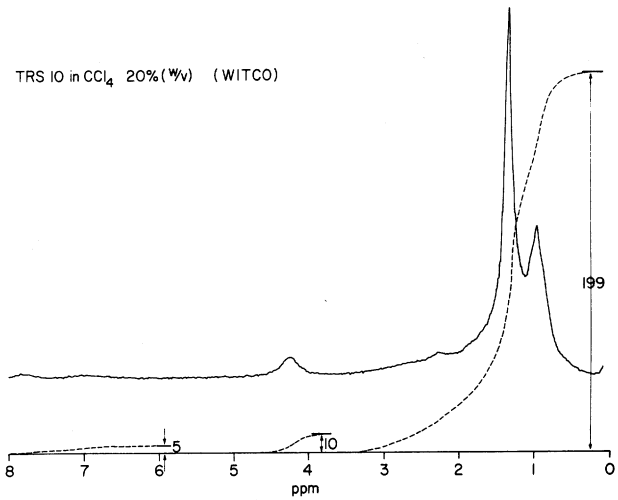

Fig. 15 - NMR spectrum of TRS 10 in CCl_4.

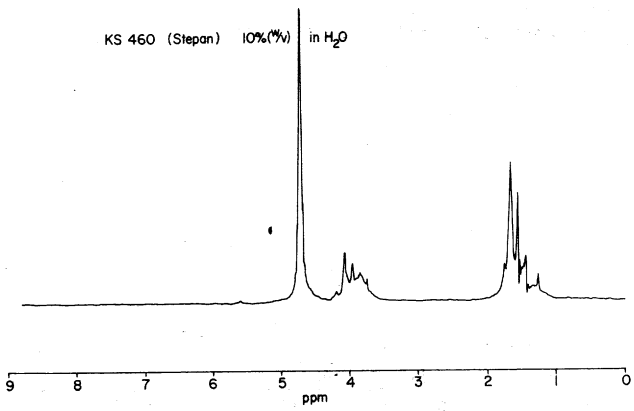

Fig. 16 - NMR spectrum of KS 460.

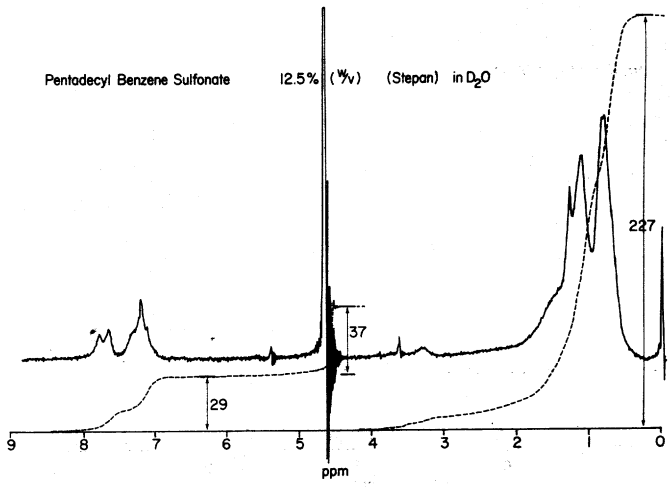

Fig. 17 - NMR spectrum of pentadecyl benzene sulfonate.

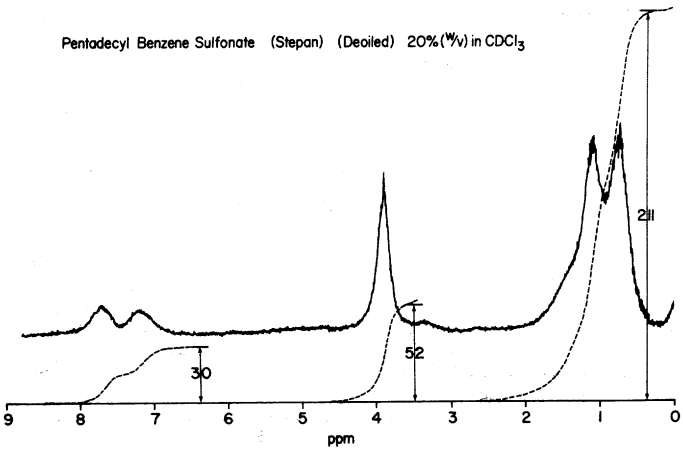

Fig. 18 - NMR spectrum of pentadecyl benzene sulfonate (deoiled).

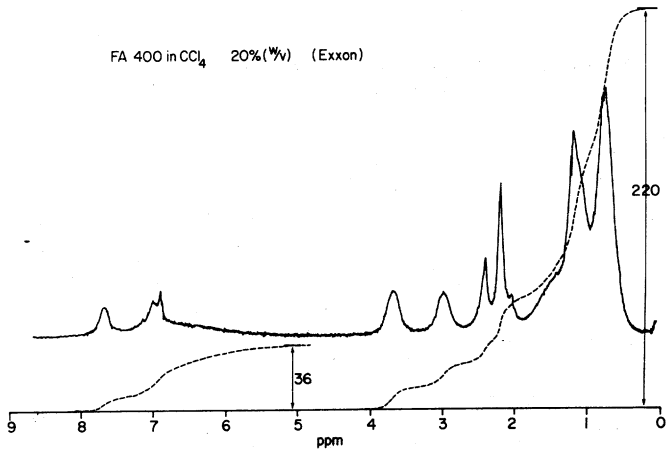

Fig. 19 - NMR spectrum of FA 400 in CCl_4.

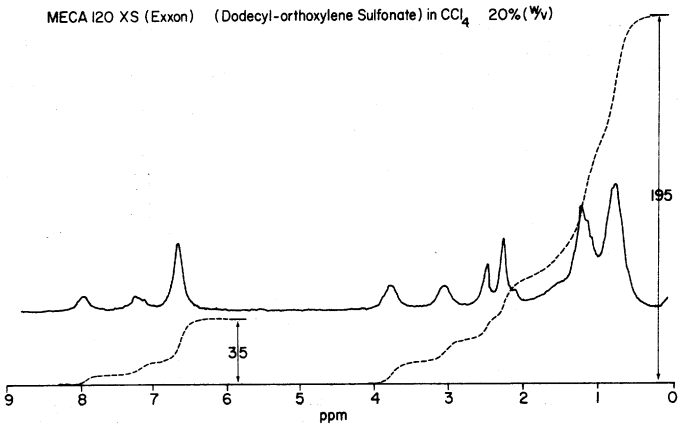

Fig. 20 - NMR spectrum of MECA 120 XS.