

The Characterization of Nonionic Surfactants by NMR¹

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Abstract

The methods currently reported in the literature for the characterization of nonionic surfactants are usually applied to one portion of the molecule and require a knowledge of the other portion for complete identification. This indirect approach leaves much to be desired. A simple, rapid, and more direct method of characterization is to measure the proton signal intensity in high resolution nuclear magnetic resonance (NMR) spectra. This method determines the hydrophile to hydrophobe ratio without requiring standard samples for calibration or a prior knowledge of the hydrophobe. In addition, this method will frequently give much valuable information about the identity of the hydrophobe, such as the average chain length, the degree of branching, and the type of aromatic substitution, if any. This method has been applied to the characterization of the common types of commercial polyethylene oxide condensates. The application of NMR to the analysis of formulated detergent products is also discussed.

Introduction

THERE ARE MANY METHODS for the characterization of nonionic surfactants reported in the literature. Infrared absorption is a simple and rapid way to identify the nonionic as a whole (3,4,5). It can also be used to determine the ratio of hydrophile to hydrophobe, providing the hydrophobe is known and suitable standards exist. Cloud point is another method for determining the hydrophile to hydrophobe ratio. There are many different ways to obtain the cloud point (1,7,8); but in order to correlate it with the hydrophile to hydrophobe ratio, you must establish a calibration curve for each different hydrophobe. Methods using measurements of density (7) or refractive index (2) have also been reported; but these, too, require standards and calibration curves for each nonionic.

The preferred chemical method uses hydriodic acid to split the ether linkages and liberate iodine which is titrated with a standard thiosulfate solution (6). This approach cannot be used for nonionics containing amine, amide, or mercaptan hydrophobes.

A simple, rapid, and more direct method of characterization is to measure the proton signal intensity in high resolution nuclear magnetic resonance (NMR) spectra. This method determines the hydrophile to hydrophobe ratio without requiring standard samples for calibration or a prior knowledge of the hydrophobe. In addition, this method will frequently give much valuable information about the identity of the hydrophobe, such as the average chain length,

the degree of branching, and the type of aromatic substitution, if any.

Theory of NMR Spectroscopy

Nuclear magnetic resonance spectroscopy is based on the fact that nuclei of many atoms have an associated magnetic moment; thus they are affected by any applied magnetic field. When placed in a magnetic field, they align themselves in certain definite orientations with respect to the field. These different orientations have different energies. By applying an oscillating field in the radio frequency range, we may excite these nuclei and detect transitions between these energy levels. This energy change is amplified and recorded.

The value of the magnetic field seen at a given nucleus depends on the electronic structure around the nucleus; thus nuclei of a given isotope, in this case the proton or H¹ nucleus, absorb energy at different frequencies when in different electronic environments. If there are several hydrogen atoms in a compound, every one that has an appreciably different electronic environment will produce a peak in the NMR spectrum. The difference between the frequency of an isolated hydrogen atom taken as a reference point and a particular hydrogen atom in a given compound is defined as its chemical shift.

The chemical shift and the spin coupling (the splitting of a signal from a single nucleus or group of closely related nuclei into more than one peak) give much qualitative structural information. Quantitative measurements can be made of the signal intensity. The intensity of the NMR signal is dependent only on the number of nuclei giving the signal. This fact allows the use of NMR for quantitative applications without requiring pure standards and calibration curves.

Experimental Procedures and Data

The studies reported in this paper were made using a Varian Associates HR-60 high resolution nuclear magnetic resonance spectrometer with associated integration system. This instrument operates at 60 megacycles per second and with a magnetic field of 14092 gauss. Spectra are obtained by holding the oscillator frequency constant and varying the current to the large d-c magnet, thus sweeping the desired portion of the magnetic field.

Accuracy and Precision. With the fairly straightforward structures found in the commercially pure nonionics we studied, the accuracy and precision should be limited only by the electronic integrator and its associated recorder. This is about $\pm 1\%$ with our equipment.

Samples for this study were run as 50% solutions in carbon tetrachloride, a solvent containing no hydrogen atoms. The sample is placed in a small glass

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tube to which is added the reference standard tetramethylsilane. The hydrogen atoms of tetramethylsilane are equivalent; thus it shows a single sharp line at a relatively high value of the magnetic field. This line is assigned a tau value of 10.00, and the positions of the other signals are assigned by their distance from the tetramethylsilane signal in ppm of the applied magnetic field.

The tube containing the sample is placed between the poles of the magnet. The current to the magnet is varied, and the NMR spectrum is recorded. This technique is rapid, requiring about 30 min per determination. Only about 0.05 ml of sample is required, and this can be recovered by evaporating the solvent. The results obtained are average values; thus having a sample which is a combination of homologues and polymers is no hindrance. Water, glycols, and any other materials giving proton signals in the regions we are examining will interfere.

We have applied this technique of quantitative high resolution proton nuclear magnetic resonance to the characterization of the common types of commercial nonionics. The samples we studied were polyethylene oxide condensates of hydrophobic bases such as amides, amines, mercaptans, and polypropylene oxide as well as the more common condensates with acid, alcohol, and alkylphenol hydrophobes.

Alkylphenol Ethoxylates. The alkylphenol-ethylene oxide condensates demonstrate the great amount of information obtainable by this technique. Figure 1

being a quantitative measure of the number of protons giving a signal. Since we know the aromatic signal comes from four protons, we can calculate the number of protons in each side chain. Doing so, we find this sample is nonylphenol condensed with 1.5 moles of ethylene oxide. The spectrum further indicates that the aromatic substitution is para and that the alkyl side chain is highly branched, probably polypropylene in origin.

Table I shows data obtained from a number of different ethoxylated alkylphenols, including octyl-, nonyl-, and dodecyl-phenol condensed with varying amounts of ethylene oxide. In every case, the NMR results show close agreement with the manufacturer's data.

TABLE I
Alkylphenol Condensates

Sample	Alkyl chain		C ₂ H ₄ O units	
	NMR	MFG	NMR	MFG
Igepal CO-210.....	C _{8.8}	C ₉	1.5	1-2
CO 530.....	C _{9.1}	C ₉	6.3	6
CO 630.....	C _{9.3}	C ₉	9.5	9-10
Triton X-100.....	C _{8.0}	C ₈	9.9	9-10
Sterox DF.....	C _{11.8}	C ₁₂	6.3

Alkyl Ethoxylates. Unfortunately, all of the nonionic types we studied do not give so much information. Both the Pluronic type products and the ethoxylated alcohols present some minor difficulties. Figure 2 shows the NMR spectrum of an ethoxylated

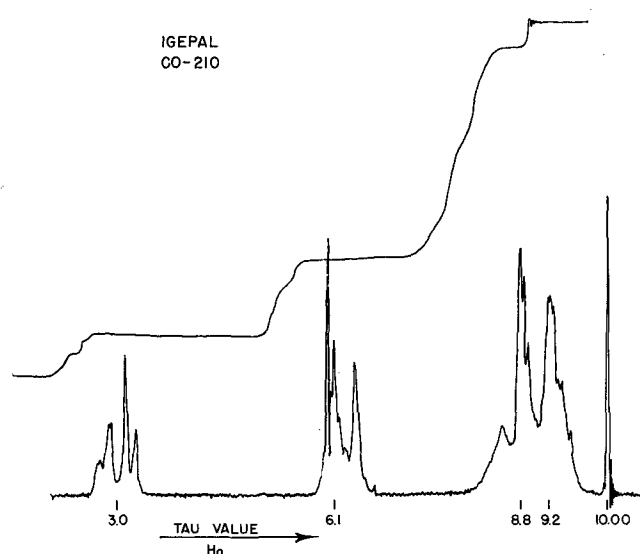


Fig. 1. Typical NMR spectrum of the alkylphenol-ethylene oxide condensate type of nonionic surfactant. Printed above the spectrum is its integral.

shows the NMR spectrum of a typical nonionic of this type. In addition to the line from tetramethylsilane at 10.00 tau, there are three well separated groups in this spectrum. The lowest field group (3.0 tau) is due to protons directly attached to an aromatic nucleus. Spin-coupling causes this signal to split into several peaks. This particular signal structure indicates para-substitution.

The middle grouping (6.1 tau) is from the protons of the ethylene oxide chain plus the terminal hydroxyl proton. The high field grouping is from the protons in the alkyl side chain. Printed above the spectrum is its integral, each step in the integral

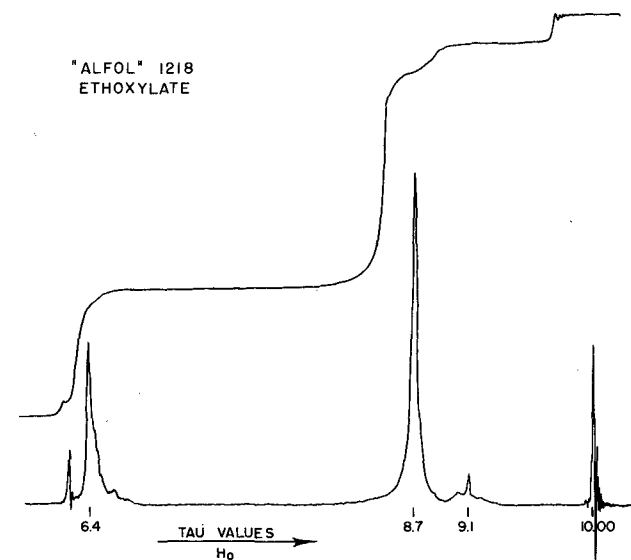


Fig. 2. Typical NMR spectrum of a straight-chain primary alcohol-ethylene oxide condensate type of nonionic surfactant.

“ALFOL” 1218 alcohol. As expected, the signal from the O-CH₂ of the alcohol falls under the signal from the ethylene oxide units; thus we can directly calculate only an approximate ratio between hydrophile and hydrophobe; however, if the signal from the methyl group protons is sufficiently resolved from the methylene signal and something is known about the branching in the alcohol, the intensity of the methyl proton signal can be used to calculate the mole ratio.

Table II shows data obtained on four ethoxylated alcohols. The mole ratio was calculated on the oleyl alcohol sample by using the NMR signal from the protons adjacent to the double bond. The lauryl

alcohol sample was calculated from the methyl proton signal, and the "ALFOL" alcohols were calculated from prior knowledge of the alcohol molecular weight.

TABLE II
Alcohol Ethoxylates

Sample	Hydrophobe	C ₂ H ₄ O units	
		NMR	MFG
Emulphor ON-870.....	Oleyl alcohol	21	23
Brij 30.....	Lauryl alcohol	4.2	4
RWW-1217-24.....	"ALFOL" 1218	3.1	3.0
RWW-1217-24-1.....	"ALFOL" 1218	9.0	8.6

The other product type that presented some difficulties was the condensation product of ethylene oxide with propylene oxide. A typical spectrum is shown in Figure 3. The signal at 8.9 tau is from the

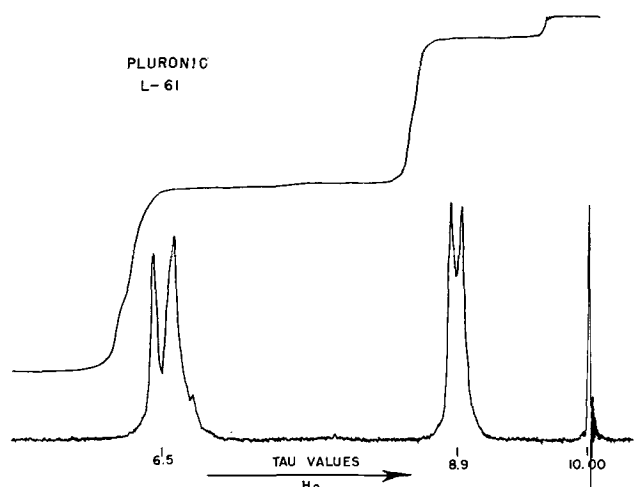


FIG. 3. Typical NMR spectrum of the condensation product of ethylene oxide with propylene oxide.

methyl group protons of the propylene oxide units, while the signal at 6.5 tau is due to protons on carbon atoms which are attached to oxygen. In this case, we can determine the ratio of propylene oxide to ethylene oxide but cannot assign a definite number of protons to either of these signals.

Table III shows the ratio of propylene oxide to ethylene oxide (in weight per cent) for a series of these polymers. You will note a considerable difference between our data and the manufacturer's data; however, if we combine our NMR values for per cent of ethylene oxide with the manufacturer's values for the molecular weight of the final products (2,000, 2,500, and 2,900, respectively), we get very good agreement with the manufacturer's value for the molecular weight of the hydrophobic base.

TABLE III
Ethylene Oxide—Propylene Oxide Block Polymers

Sample	Wt. % C ₂ H ₄ O		M.W. of C ₃ H ₆ O Base	
	NMR	MFG	NMR	MFG
Pluronic				
L-61.....	13.7	10	1725	1750
L-62.....	30	20	1750	1750
L-64.....	41	40	1700	1750

Miscellaneous Hydrophobes. Table IV summarizes the data obtained when we examined the ethylene oxide condensates of acids, amines, amides, and mercaptans. None of these products presented any difficulty, and we were able to determine the molecular weights of the hydrophobe and hydrophile chains as well as the mole ratio.

TABLE IV
Other Ethylene Oxide Condensates

Sample	Hydrophobe	C ₂ H ₄ O units	
		NMR	MFG
Emulphor VN-430.....	Oleic acid	6.2	6
Sterox CD.....	Tall oil acid	13	12
Ethomeen C/25.....	Coco amine	14	15
Ethomid 9/15.....	Oleamide	5.5	5
Sterox SK.....	Mercaptan	7.6

In addition to these nonionic surfactants which we studied, we have also applied this technique to nonionics and sulfated "nonionics" which were separated from commercial detergent formulations. These products were removed from the formulations by the usual extraction and ion exchange techniques. Table V lists some typical analyses. The two products with low mole ratios of ethylene oxide to hydrophobe were present as sulfates. We hydrolyzed them before recording their NMR spectra. In the future, however, we plan to look at some of these sulfated ethoxylates as such.

TABLE V
Ethoxylates from Detergent Formulations

Sample	Hydrophobe	C ₂ H ₄ O units
AN 5932.....	Nonylphenol	9.5
AN 5443.....	Nonylphenol	4.0
AN 5445.....	Nonylphenol	10.6
AN 6010.....	Nonylphenol	4.6
AN 7677.....	Tridecanol	9.5

Summary

In summary then, we have described a simple, rapid, and fairly direct method for the characterization of nonionic surfactants. Quantitative measurement of the proton signal intensity in high-resolution nuclear magnetic resonance spectra determines the hydrophobe to hydrophile ratio without requiring standard samples for calibration or a prior knowledge of the hydrophobe. Further, with most product types, this technique actually permits calculation of the average molecular weights of both portions of the molecule. The technique is nondestructive, and only a small amount of sample is required.

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