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Determination of the Molecular Weight Distribution of Polyether Surfactants

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Synopsis—Many of the characteristics which are important in formulating with POLYETHER SURFACTANTS are dependent on MOLECULAR WEIGHT DISTRIBUTION. The determination of the molecular weight distribution of a commercial quaternary ammonium polyether surfactant is reported. The intermediate tertiary aminopolyether alcohol which contains polypropylene glycol as a by-product has a distribution identical to that of the quaternary products and was used in the analyses.

The amine and glycol fractions were separated by esterification of the mixture, which permits partitioning of the esterified amine and glycol fractions into different solvents. The makeup of each fraction was determined by integrated programmed GAS CHROMATOGRAPHY. In addition, the aminopolyether fraction was analyzed by a combination of MASS SPECTROSCOPY and NUCLEAR MAGNETIC RESONANCE.

The amine fraction was found to have a symmetrical distribution of molecular weights, while the glycol fraction had more high molecular weight than low molecular weight components. This method for determination of the molecular weight distribution is readily adapted to other polyether surfactants.

Introduction

Polyether surfactants are employed in a variety of cosmetic products. In most cases, the average molecular weight of the polyether is

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specified and surfactants with different molecular weights have different properties. These include water solubility, physical appearance, viscosity, and emulsifying properties. Once a particular average molecular weight is chosen, the property which most influences its performance is the molecular weight distribution. In most cases, one would prefer a narrow distribution since this would insure more uniform characteristics from the material chosen.

The molecular weights of polymers can be determined by chemical or physical methods of functional group analysis, by measurement of the colligative properties, light scattering, or ultracentrifugation, or by measurement of dilute solution viscosity. The colligative properties which are used to determine molecular weights are based on vapor pressure lowering, boiling point elevation, freezing point depression, and the osmotic pressure. Of these four methods, the most useful is osmotic pressure since the largest effect is observed in this measurement. End-group analysis as well as colligative methods give the number-average molecular weight (Mn). The number-average is very sensitive to changes in the weight fractions of low molecular weight species. In contrast, the method of light scattering to determine molecular weight gives the weight-average molecular weight (Mw), since the amplitude of scattered light is proportional to the mass of the scattering particle. The weight-average is particularly sensitive to the presence of high molecular weight species. For example, if equal weights of molecules with $M = 10{,}000$ and $M = 100{,}000$ are mixed, $Mw = 55{,}000$ and $Mn = 18{,}200$; if equal numbers of each kind of molecule are mixed, $Mw = 92{,}000$ and $Mn = 55{,}000$. Mw is always greater than Mn except for a monodisperse system. The ratio Mw/Mn is a measure of the polydispersity of the system. For polymers with a very narrow molecular weight distribution, this value will approach one.

It can be seen from the above that the molecular weight alone is not very useful when dealing with a polymeric material. The property of interest is the molecular weight distribution. Certain characteristics, such as solubility, which are important in the formulation of a product, require that one knows what type of distribution he is dealing with. This knowledge is essential for determining what molecular weight range of a particular polymer one is interested in and whether a particular sample from a supplier meets specifications.

The literature contains several references to work on the determination of the molecular weight distribution of polyethers. Considerable

work has been done on polyethylene glycol; very little has been reported on polypropylene glycol.

Gildenberg and Trowbridge (1) used gas-liquid chromatography to separate ethylene oxide adducts of fatty alcohols. The hydroxyl groups were converted to the acetate esters. This increased the stability of the molecule to high temperatures and permitted temperature programming, enabling them to obtain separate peaks for adducts with up to 13 ethylene oxide units.

Calzolari (2) studied the molecular weight fractionation of polyethylene glycol by gas chromatography. Of several derivatives of the polyethylene glycol which were tried, the trimethylsilyl derivative was selected because it had the highest volatility and thermal stability and the lowest energy of absorption on the support, thus making it the most suitable for the analysis of polyethylene glycol products with a molecular weight of less than 1000.

Withers (3) has also reported on the gas chromatography of polyethylene glycols. Identification of the series of polyethylene glycols was made by running the first four members of the series since these were available as pure materials. The assumption was then made that successive peaks following these four each represent an increment of one ethylene oxide residue since the standards correspond to the first four peaks.

Ludwig (4) used a variety of techniques for the separation of oligomers of ethylene oxide and propylene oxide adducts of alkylphenols. The procedures applied were gas chromatography on derivatives, thin-layer chromatography, and gel permeation chromatography. In addition, nuclear magnetic resonance spectroscopy was used to determine the ethylene oxide/propylene oxide ratio in a copolymer. This work gave the average molecular composition, but did not concern itself with the exact molecular weight distribution.

Another technique which has been widely used successfully to determine molecular weight distributions is gel permeation chromatography. One advantage of this method is that it permits one to obtain separations in molecular weight ranges far exceeding 1000. The advent of high-speed liquid chromatography has done much to eliminate one of the drawbacks of column chromatography, namely, the time involved for an analysis. The area of gel permeation chromatography is a very broad field in itself. An excellent monograph by Determann (5) describes its varied applications.

Experimental and Results

In the course of investigating various surfactants for possible use in cosmetic formulations, Emcol CC-9®,* a quaternary ammonium polyoxypropylene alcohol, was obtained. It is prepared by autoclaving diethylamine with propylene oxide in the presence of base (Fig. 1). The resulting tertiary aminopolyether alcohol polymer contains as a by-product polypropylene glycol, which results from self-condensation of the propylene oxide in the presence of water. This mixture is then quaternized with methyl chloride to prepare the Emcol CC-9.

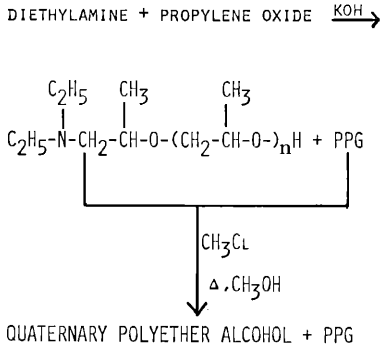

Figure 1. Preparation of Emcol CC-9

In the work-up of the quaternary product, only the excess solvent and methyl chloride are pumped off. Thus, the tertiary aminopolyether alcohol and the quaternary product will have the same molecular weight distribution. Therefore, in order to determine the molecular weight distribution, a sample of the tertiary aminopolyether alcohol was obtained which was actually a mixture of tertiary aminopolyether alcohol (AP-OH) and polypropylene glycol (PPG). In order to separate the two, the mixture was acetylated as shown in Fig. 2.

The hydroxyl number of the Emcol CC-9 tertiary amino alcohol mixture was determined to be 2.17 meq of hydroxyl per gram. To a refluxing solution of 2.81 g (35.8 meq) of redistilled acetyl chloride in 20 ml of anhydrous ether under nitrogen atmosphere was added 15 g (32.5 meq) of Emcol CC-9 amine slowly over a period of 75 min. The pale yellow solution was refluxed an additional 2½ hours. It was then cooled to room temperature, made more acidic with 2*N* HCl, and added to 40 ml of water. After extraction twice with ether, the aqueous layer was brought to pH 9.5 with 5*N* NaOH. It was then extracted several times

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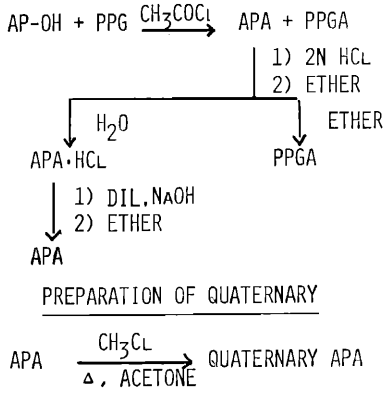


Figure 2. Preparation of aminopolyether acetate (APA)

with ether. Both ether extracts were dried over sodium sulfate and the ether was removed in vacuo.

The acidic ether extract yielded 1.9 g of polypropylene glycol acetate. The basic ether extract yielded 13.5 g of aminopolyether acetate. The yield of combined product was quantitative and from the recovery of polypropylene glycol acetate it was determined that the starting mixture contained about 10% polypropylene glycol.

Proof of separation of the two components can be confirmed from the infrared spectra of the products. These spectra were obtained on a Beckman IR-10 spectrophotometer as smears on NaCl plates. The glycol acetate has a band at 1740 cm^{-1} due to ester carboxyl (C=O) and no band at 3400 cm^{-1} where hydroxyl shows up in the starting material. In addition, a qualitative test for nitrogen by the sodium fusion method was negative. On the other hand, the amino acetate has bands at 2805 cm^{-1} due to the diethylamino group; at 1740 cm^{-1}, due to the ester carboxyl; and none at 3400 cm^{-1}.

The separated samples of the glycol acetate and amino acetate were then analyzed by gas chromatography. A Varian Model 1860 gas-liquid chromatograph, equipped with flame ionization detectors, was used. The column, 5 ft $\times$ 0.125 in. stainless steel, contained 3% SE-30 on Varaport (100/200 mesh). Helium carrier flow was 25 ml/min. The column was programmed from 120°C at 15°/min for 5 min; 6°/min for 10 min; and 4°/min until 325°C and held. The relative areas of the observed peaks were measured by an electronic digital integrator. A complete analysis would obviously require identification of all the components in the mixture. However, some conclusions can be drawn as to the composition of the two separated materials.

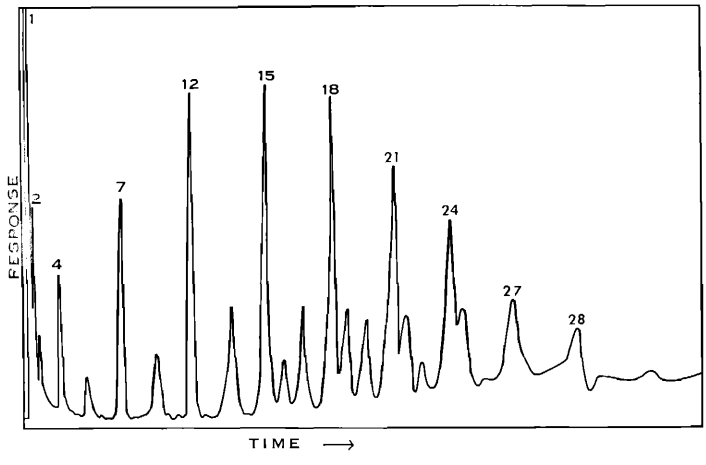


Figure 3. Gas chromatogram of polypropylene glycol acetate (PPGA)

An examination of the glycol acetate fraction in Fig. 3, neglecting the first peak which is due to some residual ether in the sample, shows that the distribution of the peak areas is not symmetrical. There is a higher percentage of the high molecular weight than the low molecular weight components. The major peaks from No. 15 and further each account for about 8% of the total area. The peak areas increase until peak No. 15 and then remain at that level through peak No. 28. The distribution of peak areas in this sample is shown in Table I.

The structure of the lowest molecular weight components of the glycol fraction has been determined by comparison of the gas chromatography retention times with those of standards. Samples of propylene glycol,

Table I

Area Distribution for the Polypropylene Glycol Acetate

Peak No.	Area Percentage
2	1.4
3	1.2
4	1.9
7	3.3
12	5.8
15	7.7
18	8.7
21	8.2
24	8.3
27	7.8
28	8.1

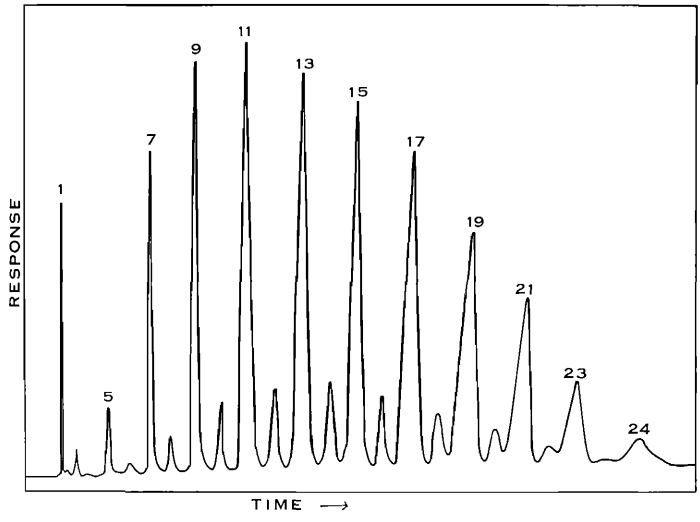


Figure 4. Gas chromatogram of aminopolyether acetate (APA)

dipropylene glycol, and tripropylene glycol were acetylated and their retention times were compared to those of the peaks in the spectrum of the glycol acetate fraction. In addition, a small amount of each of the standards was added to separate samples of the glycol acetate and increased intensity of the peak corresponding to the standard was observed. In this way, peaks 2, 3, and 4 have been identified as propylene glycol diacetate, dipropylene glycol diacetate, and tripropylene glycol diacetate, respectively. This confirms that the low molecular weight glycols are a small part of the mixture.

The chromatogram of the aminopolyether acetate is shown in Fig. 4. Determination of the area of each of the peaks shows that in this case a symmetrical distribution of peak areas is obtained. The peak area percentage gradually increases and reaches a maximum at peak No. 15, which accounts for 13.5% of the total area. From that point, the peaks gradually decrease in area. The distribution of peak areas in this sample is shown in Table II.

In order to determine the actual composition of individual fractions, three consecutive major fractions (namely, peaks 5, 7, and 9) were isolated using preparative gas chromatography. Proof of their structure was then determined by a combination of mass spectroscopy and nuclear magnetic resonance. Mass spectra were obtained on a Varian CH7 mass spectrometer with batch inlet with a source temperature of 250°C. The ionizing potential was 70 eV with an accelerating potential of 3 kV. NMR spec-

Table II
Area Distribution for the Aminopolyether Acetate

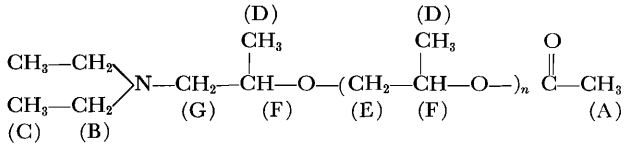
Peak No.	Area Percentage
1	0.9
5	0.7
7	2.8
9	6.4
11	10.3
13	12.5
15	13.5
17	12.8
19	10.5
21	7.7
23	5.3
24	2.8

tra were obtained on a Varian T60 NMR spectrometer on $CdCl_3$ solutions with tetramethyl silane as internal standard.

The mass spectra of the three isolated fractions were determined on a gas chromatograph–mass spectrometer interface with a computer printout. If such an instrument is available, it is not necessary to isolate samples.

The highest fragment is obtained at m/e 274 for sample No. 1; at m/e 332 for sample No. 2; and at m/e 390 for sample No. 3. The difference in mass between the three fractions is 58, which is equal to the mass of the propylene oxide repeating unit. This and the fact that the decomposition patterns are similar and vary in a regular manner indicate that the samples are three successive members of a homologous series. Table III shows the structural formula for the aminopolyether acetate.

Table III
Structural Formula of the Aminopolyether Acetate (APA)



n	Mol Wt	No. of Protons
0	173	19
1	231	25
2	289	31
3	347	37
4	405	43
5	463	49

It can be seen that the three samples correspond to the formula where $n = 2, 3, 4$ and that, in each case, the highest fragment observed is not the molecular ion but one corresponding to a mass loss of 15, or one CH_3 group.

Confirmation of the mass spectroscopic results was sought by an examination of the 60 Megahertz proton spectra of samples 1 and 3. Because of sample impurities demonstrated in the mass spectroscopic analysis the NMR results, by themselves, are not unequivocal. However, they complement the mass spectroscopic results, and the analysis will be shown here to illustrate the principle.

After the spectra were determined, two carefully measured integrals were recorded for each compound and the total proton counts and relative integrals for the various proton types were calculated from the average of the two integrations.

There are two ways to determine the structure of the compound, each of which will be illustrated with one of the samples. In the structural formula in Table III, the proton types corresponding to the various signals in the spectrum have been indicated. The spectrum of sample 1 is shown in Fig. 5. The reference signal is the singlet at 2.0 ppm, which must be assigned to the acetate methyl protons (the protons labelled A). The number of these A protons will not increase, but as the chain length grows the number of E and F protons between 3.2 and 3.8 ppm will increase by 3 for every added propylene oxide unit. If the integral for the A protons is 3, then the integral for the E and F protons is 6.3. If $n = 1$, there are 4 E and F protons, while if $n = 2$, there are

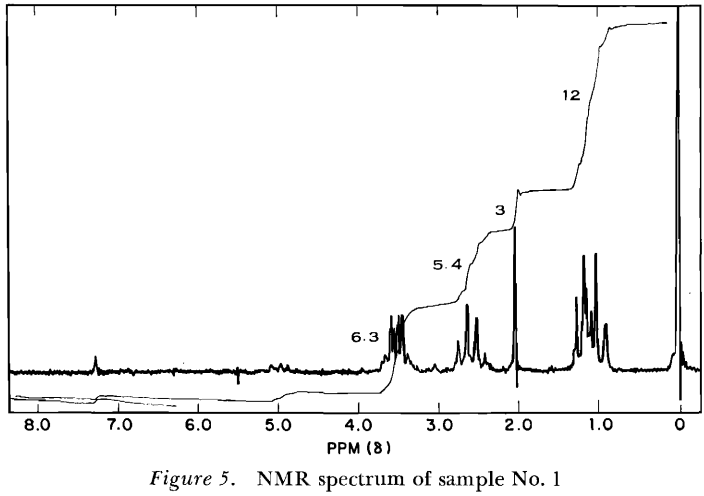


Figure 5. NMR spectrum of sample No. 1

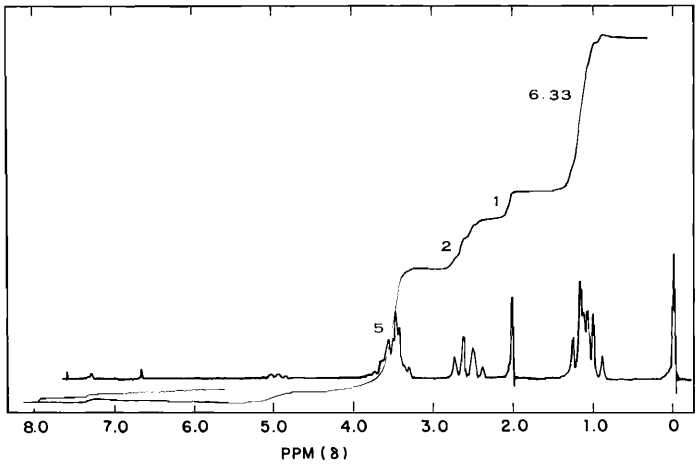


Figure 6. NMR spectrum of sample No. 3

7 E and F protons. Thus, as stated, this information complements the mass spectroscopic data.

Alternatively, the relative integrals for all the protons can be determined and the integral at 2.0 ppm set equal to 3 protons. In this way, the number of protons in each integral and the total proton count for the molecule can be obtained. This is illustrated in Fig. 6, which shows the spectrum of sample No. 3. The numbers to the left of the integration trace are the relative integrals. If these numbers are multiplied by 3 and the number of protons is summed, one gets $15 + 6 + 3 + 19 = 43$ protons which corresponds exactly to the proton count of the molecule where $n = 4$.

Conclusion

A commercial mixture of two different types of polymers has been separated. In the case of the polypropylene glycol, it was determined that the distribution was nonsymmetrical and, through the use of appropriate standards, three successive members of the gas chromatogram were identified. The aminopolyether acetate, on the other hand, did have a symmetrical molecular weight distribution, and after isolating three successive fractions, proof of their structures and the fact that they were indeed consecutive members of a series was accomplished by a combination of mass spectroscopy and nuclear magnetic resonance.

The usefulness of this method for determining molecular weight distributions should be stressed. A gas chromatograph–mass spec-

trometer interface is the simplest most direct way to separate and analyze a complex mixture, although gas chromatography–mass spectroscopy interface instruments are still beyond the budgetary capability of most laboratories. However, most laboratories own or have easy access to a nuclear magnetic resonance spectrometer and have some facilities for chromatographic separation on a preparative scale. These may include preparative gas chromatography, thin-layer, or column chromatography. If one separates and collects fractions of a mixture, the fractions can be derivatized such as by acetylation on the terminal hydroxyl group. One now has a handle, which is easily located in the NMR spectrum and whose signal strength remains constant over all components of the mixture. One can then easily compare its signal to the signals which increase with increasing chain length.

For polyether surfactants of molecular weight up to about 1200, this is a simple way of determining the chain length of any fraction. This information combined with the chromatographic separation data should give a complete molecular weight distribution.

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