Molecular Weight and EON Distribution of Industrial Polyethoxylated Surfactants by High Performance Size Exclusion Chromatography

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Abstract: Polyethoxylated nonionic surfactants were analyzed by high performance size exclusion chromatography (HPSEC) using different pore size Ultrastyragel columns with tetrahydrofuran (THF) as mobile phase. Not only does HPSEC provide molecular weight distribution but also ethylene oxide number (EON) average estimation over a wider EON range. In this work, the analysis is extended to others nonionic ethoxylated surfactants and the application of this procedure for manufacturers and formulators is discussed. Calibration plots using polystyrenes standard and three polyethoxylated surfactants groups exhibit an excellent linearity and parallelism with the same slope indicating that calibration with the Q-factor approach can be used to calculate molecular weight and EON average in this type of samples.

Keywords: High performance size exclusion chromatography, EON distribution, polyethoxylated surfactants, Molecular weight, EON distribution of nonionic surfactants

INTRODUCTION

The polyethoxylated compounds have held a prominent position in the field of nonionic surfactants in the past 40 years. They are used in household products such as liquid dishwashing formulations and hard surface cleaners; and...
cleansers for textiles, leather, and plastics, particularly in systems with high
electrolyte content. They are used extensively in the oil industry, e.g., as emul-
sifiers in drilling fluids and heavy crude emulsions (1), and have been
proposed as tension-lowering surfactants for enhanced oil recovery (2, 3).
Nonionic surfactants of the polyether type are synthesized by adding
ethylene oxide to substances with a reactive hydrogen atom, such as alkylphe-
nols (2). During the ethoxylation process, the adduction randomness results in
a mixture of oligomers with different degrees of ethoxylation. As a conse-
quence of its ethylene oxide number (EON) distribution, which often
follows a Poisson law (4), a commercial surfactant may contain substances
with widely different properties. In the presence of both an oil and a water
phase, this can result in an independent solution behavior of each substance
that may cause problems in certain applications and formulations.

Various chromatographic methods were proposed for the analysis of
polyethoxylated surfactant. Most of these studies were performed by both
reversed and normal-phase high performance liquid chromatography
(HPLC). Octadecyl- or octyl-sylane columns were used for such separations
(5–9). Silica gel (6, 7, 10–12) and silica with chemically bonded nitrile
(6, 7), diol (7), and amino phases (7–9,13–18) were also tested as column
packing in normal-phase HPLC separation. However, the main problem
in the analysis of mixtures of oligomers by HPLC is the effective fractionation
of chains with widely different affinities. This characteristic makes the
analysis of EON distributions higher than 50 difficult. Related to detection,
some publications on HPLC analysis have reported that the ethoxylated alkyl-
phenol surfactant oligomers can be detected by ultraviolet (UV) absorbance or
fluorescence techniques and by refractive index (19–21).

Normally, HPSEC is used as an analytical procedure for separating small
molecules by their difference in size and to obtain molecular weight averages
(Mn and Mw) distribution We reported in a previous work (22) information
about molecular weight distribution (MWD) and EON distribution of
samples with different chain sizes. The primary retention factor in this
technique is the fraction of the pore volume of the column packing that is acces-
sible by the molecule. Commonly, HPSEC is performed with a sensitive
detector, and the sample molecular weight is determined by comparing the
elution volume of the peak maximum with those of a series of known
molecular weight standards. On the other hand, in some works (22, 23)
Q-factor is taken as the molecular size per extended chain length in
angstroms, and it is assumed that a given retention volume corresponds to a
given known angstrom length (i.e., polystyrene), the molecular size for any
unknown polymer can be obtained by using the calibration plot. However it
seems that all trials ended in a failure to attain reliable data, and that results
were good only to provide a qualitative comparison between two substances.
Another problem in analyzing surfactants by size exclusion chromatography
(SEC) seems to come from the formation of micelles in water and other
solvents. In this system a micelle is a polymer aggregation that occurs as soon as a certain concentration, critical micellar concentration (CMC) is reached. As a matter of fact, some authors have proposed using a version of SEC, gel permeation chromatography (GPC) to estimate the extent of micelle formation (4).

Despite of the long history of application of size exclusion chromatography (SEC) to other associating systems, few works have been proposed to analyze nonionic surfactants. In fact, only a few works have been reported to characterize nonionic surfactants (24–28), in studies of surfactant-polymer interactions (29) and with surfactants mixtures (26, 30, 31) using HPSEC technique. Although SEC has not been applied very often in the analysis of surfactants, some advantages arise by using this technique: as the separation is governed almost exclusively by the overall size of the molecule (the hydrodynamic volume or radius of gyration) and for some applications, to a first approximation, the most important information is the functionality distribution.

Polyethoxylated surfactants can be seen as little molecules of polymers (oligomers) because they are prepared by the addition of ethylene oxide to a hydrophobic compound containing active hydrogen. Furthermore, since surfactants with higher EON oligomers are often required in wetting, detergency, and foaming applications (32), and since surfactants with EON in the 50–100 range can be considered as small macromolecules, an HPSEC approach can be a good choice to analyze alkylphenol ethoxylated with a high degree of ethoxylation and achieve good results in EON average determination. In a previous work we demonstrated that HPSEC provides an excellent EON average estimation (22); in this work we extend the studies to other families of polyethoxylated surfactants, to compare their behavior in the phenomenon of selective exclusion–permeation and to discuss some situations where this technique can provide important information.

**EXPERIMENTAL**

**Standards and Samples**

Two polystyrene standard sets from Polymer Laboratories were used: 1) a medium weight P/N 2010–0100 sample with molecular weight (MW) ranging from 580 to 3.15 × 10^6 Daltons; and 2) a low molecular weight P/N 2010–0101 sample with MW ranging from 162 to 22,000 Daltons. Each standard set contained 10 calibration samples and a verification sample. Verification samples exhibited MW of 580 and 1700 Daltons, respectively. A pure nonethoxylated nonylphenol from Aldrich was also used as a reference. Commercially ethoxylated alcohols (APX) from Etoxil (Maracaibo, Venezuela), ethoxylated terbutylphenol (tBPX) surfactants, and ethoxylated nonylphenol surfactants (NPX) from various manufacturers were tested: Makon M series from Stepan Chemicals, Igepal; CO series from Gaf Chemicals; Siponic
NP series from Alcolac; Carsonon NP series from Carson Chemicals; Alkasurf
NP series from Alkaryl Chemicals; Emulgen E9XX series from Kao Atlas,
Japan, series; and Arkopal NP from Hoechst GmbH. In the following sections,
these substances are referred to as NPX, APX and tBPX, respectively, where
X stands for the average number of ethylene oxide groups (EON) per molecule.

**HPSEC Analysis**

The HPSEC studies were performed using a Waters 510 HPLC pump, an U6K
injector, and a Perkin-Elmer series 200 refractive index detector. The data
were processed through an Action PC 5500 personal computer loaded with
Turbochrom software with a PE Nelson 900 series interface. Three different
pore size columns were used for this study: 1) Ultrastyragel 100 Å with a
low MW range from 100 to 1000, 2) Ultrastyragel 500 Å with a low MW
range from 100 to 10,000, and 3) Ultrastyragel 1000 Å with a low MW
range from 200 to 30,000. These three columns from Waters are made from
cross-linked styrene-divinyl benzene gels (30 cm × 7.8 mm I.D). These are
referred to as 100, 500, and 1000 Å columns respectively.

The selection of the eluting fluid in SEC is critical, providing that it is a
strong enough solvent, so that no other mechanism but size exclusion can
occur. As far as ethoxylated alcohols are concerned, they are soluble in
short chain alcohol (<C5), chloroform, and THF. Short alcohols cannot be
used in gel columns since they result in swelling and degradation, whereas
chloroform is more viscous and has a lower volatility than THF, so that the
latter is the selected solvent. Furthermore, THF is known to exhibit, in most
cases, the so-called “differential solvation” (33) effect. Pretreatment of the
solvent included: 1) filtration on a nonaqueous 0.45 μm Millipore filter, and
2) air scavenging by ultrasonic stirring and helium bubbling. Reference as
well as measurement solutions are prepared typically at a 0.2 wt% concen-
tration. Injected aliquot is 10 μL unless otherwise stated.

The HPSEC experiments were carried out under the following conditions,
unless otherwise stated: flow rate 1 mL/min⁻¹ and temperature, 25°C. To
avoid problems of column swelling, due to possible water contained in the
sample, they were treated prior to the injection as follows: dried in vacuum
oven, dissolved in THF, and then filtered on sodium sulfate anhydrous.

**RESULTS AND DISCUSSION**

Separation in SEC occurs on the basis of molecular size. Retention of solutes
by other mechanisms is undesirable. Choice of pore size normally is the most
significant parameter to be considered in the selection of the column, because
pore size dictates the range of molecular-weight separation. In preliminary
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trials Ultrastyragel 100 Å and 500 Å column were tested without satisfactory results. The results indicated that the selective permeation range is very small for all of the samples tested. On the other hand, the Ultrastyragel 1000 Å column showed a very high selective permeation range with an appropriate division range and symmetrical peaks. Figure 1 shows the molecular weight distribution of sample B (nonylphenol polyethoxylated with 85 EON) and sample C (polyethoxylated alcohol with 10 EON) using an Ultrastyragel column 1000 Å pore size. The polystyrene standard (A) (MW 100 K Daltons) in THF solution shows that the high molecular weight fraction is located in the exclusion zone, about six minutes, that corresponds to the exclusion zone of the column, 30,000 Daltons. The permeation zone is found with the injection of toluene (D). Also Fig. 1 shows symmetrical peaks in molecular weight distribution.

Figure 2 shows a calibration plot for polystyrene standard (A), for nonylphenol polyethoxylated (B), terbutylphenol polyethoxylated (C), and polyethoxylated alcohol (D). In a previous work (22) we demonstrated that polystyrene standard can be used for the determination of the Mw and Mm distribution of the nonylphenol polyethoxylated by applying a multiplicative Q-factor for correction purposes. Since NPX, APX, and tBPX are mixtures,
the reported molecular weight is actually the molecular weight calculated from the average number of ethylene oxide groups per molecule according to the manufacturer. It is worth remarking that the log MW vs. time graph exhibits an excellent linearity, a feature suitable for calibration. Moreover, the line slopes are exactly the same, but parallel, displaced toward smaller molecular weight. This shift is surely due to differences in the relationship between the molecular weight and the hydrodynamic volume. In effect, the polystyrene macromolecule probably has a larger gyration radius (and also larger hydrodynamic volume) than the corresponding polyethoxylated nonylphenol and polyethoxylated alcohol molecules, because the polyethylene oxide chain is known to fold on itself to form a random coil as a “ball.” Extra molecular weight is also conferred by the presence of oxygen atoms. The shift of the line of the polyethoxylated alcohols to smaller molecular size is probably due to the presence of the aromatic ring in the polyethoxylated alkylphenol chain that avoids the complete folding of the alkyl chain on itself. The parallelism of the three lines in a logarithmic scale means that there is a constant factor between the three results. Then we can use the Q-factor approach (22) as a tool to determine the molecular weight of the polyethoxylated surfactants starting from a calibration plot of polystyrene standard. It is known that for each Å in length, a polystyrene molecule weighs an average 41
Daltons (34); as a consequence, the Q-factor for the polyethoxylated surfactants is readily calculated using the following equations:

\[ M_{\text{approx}} = \frac{Q}{41.4} \times M_{\text{polystyrene}} \]  

(1)

Q-factor NPX = 41/1.24 = 33.06 \quad (2)

Q-factor tBPX = 41/1.32 = 31.06 \quad (3)

Q-factor APX = 41/1.58 = 25.95 \quad (4)

These values allows the calculation of the average MW of the polyethoxylated surfactants from the MW of the polystyrene specie with the same elution time.

Usually, for industrial purposes, the average EON is more useful than molecular weight of the polyethoxylated surfactant. Trying to study these correlations, a plot of EON vs. elution time was made. Figure 3 shows excellent correlation for the three polyethoxylated surfactant families. As expected, the curve for the tBPX falls below that of the NPX oligomers, in spite of having approximately the same number of carbons in the lipophilic chain; that is because the three t-butyl groups confer the molecule a smaller size in solution. Also, the calibration curve for the alcohols falls below the NPX and tBPX oligomers; we believe that the alkyl chain of this alcohol is folding on itself to form a ball that results in a smaller size to the chain in solution. Furthermore, Fig. 3 shows that the elution time is the average time for the elution of the chromatographic peaks and the EON is the average value for the commercial sample. The EON average value is calculated by means of a linear mixing rule based on the mole fractions (35, 36):

\[ \overline{\text{EON}} = \Sigma_i \text{mole fraction } \text{ith oligomer} \times i \]  

(5)

Figure 3. Calibration curve of log EON vs. elution time for NPX, tBPX, and APX using a 1000 Å column.
Figures 4, 5, and 6 show the molecular weight distributions (MWD) vs. area (%) of NPX, APX, and tBPX, respectively, for low ethoxylation degree (Figs. 4A, 5A, and 6A) and high ethoxylation degree (Figs. 4B, 5B, and 6B). In these figures symmetrical distributions of molecular weights are observed with a dispersion near the unit. However, the chromatogram of

![Molecular Weight Distributions](image)

**Figure 4.** Molecular weight distributions (MWD) of NPX for (A) low ethoxylation degree and (B) high ethoxylation degree. Conditions as mentioned in Fig. 1.
NP4 shows a small tail toward higher molecular weight, this is probably due to a mixture of products derived in the synthesis process. The bimodal distribution may be the result of the polymerization procedure, as shown in Fig. 7. In this figure, the Poisson distribution is not satisfactory since the samples of theoretical EON average of 100 came from the polymerization
reaction of a sample with EON 17; clearly two distributions are observed in the three samples that reduces the current EON average by several units. It is important to remark on the small fraction of high molecular weight in this figure (and consequently of high EO) that is observed for the sample.

**Figure 6.** Molecular weight distributions (MWD) of tBPX for (A) low etoxylation degree and (B) high etoxylation degree. Conditions as mentioned in Fig. 1.
that is reflected in a bigger EON average and in a the more hydrophilic behavior. In the preparation of asphaltic emulsions the samples 1ETO (national product) and 2ETO (imported product) had an acceptable behavior while the 0ETO resulted in stability problems.

As other applications of our HPSEC method, different commercial nonylphenol and alcohol polyethoxylated surfactants were analyzed. Table 1 summarizes the average EON and the molecular mass averages for several polyethoxylated surfactants that were obtained with different SEC calibrations as described previously. The average EON value computed from HPSEC data matches, pretty well, the manufacturer’s estimate and the available HPLC data (35, 37, 38). The calculated molecular weights are also in good agreement with other reliable information, say within a 10% analytical error level in most cases. Table 1 also reports the data dispersion, i.e., the ratio of the weight and number means (D = Mw/Mn). The computed values range from 1.0 to 1.4, as expected from the synthesis mechanism.

**CONCLUSIONS**

Use of HPSEC allows the determination of the molecular weight and the average EON distribution of a mixture of surfactants. Although it does not match the single oligomer separation attained by gradient mode HPLC, it has several advantages over HPLC techniques. First, it requires less expensive equipment and second,
it gives fairly good results as far as the average EON is concerned. Finally, it provides the best estimate for highly ethoxylated surfactants.

In formulation technology with nonionic surfactants, this developed method, HPSEC, would be useful because it allows us to obtain, not only molecular weight distribution, but also EON average information on possible mixture of products and the possible polymerization procedure.

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