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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

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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 emulsifiers 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 alkylphenols (2). During the ethoxylation process, the adduction randomness results in a mixture of oligomers with different degrees of ethoxylation. As a consequence 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 alkylphenol 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 accessible 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 micelar 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-divynil 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% concentration. 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 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 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.

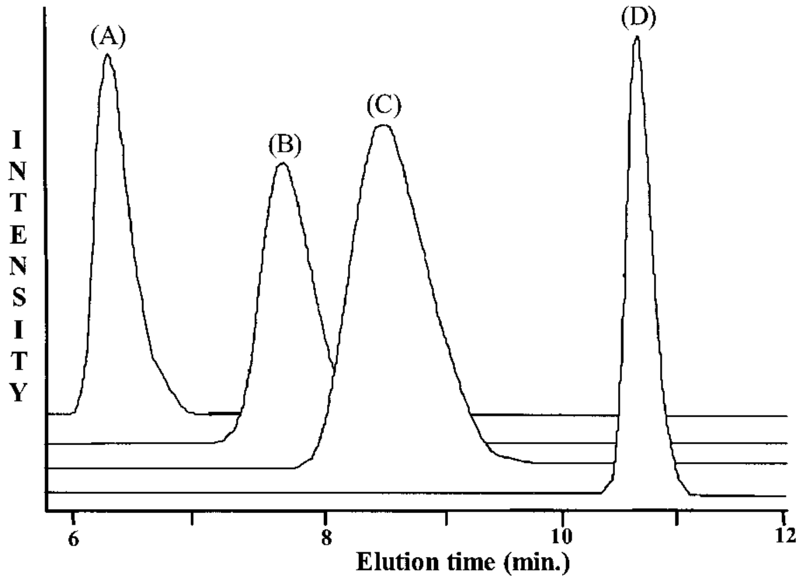

Figure 1. Selective permeation range of Ultrastyragel 1000 Å column for polyethoxylated surfactants (B) NP85 and (C) AP10 determined with a polystyrene standard (A) MW = 106.00 and toluene (D). Conditions: mobile phase THF 1 mL/min, detection RI 8X, temperature 25°C.

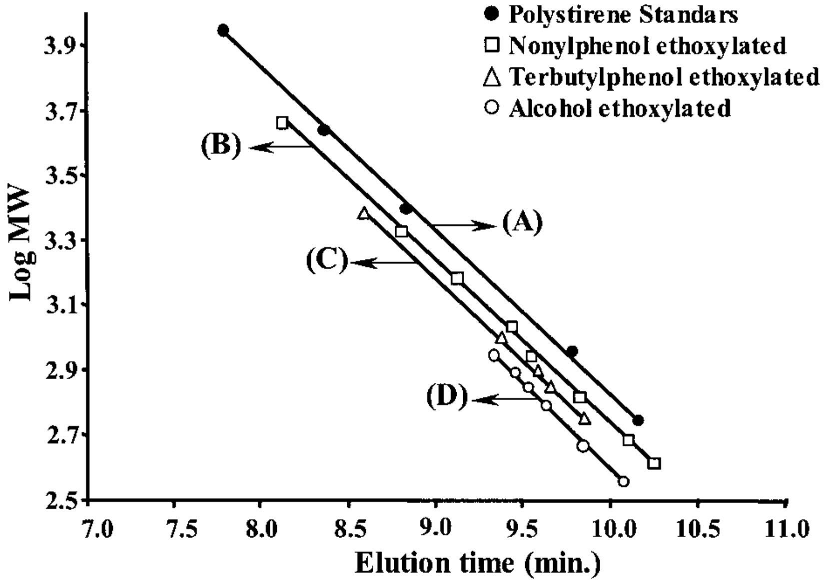

Figure 2. Comparison of calibration curves Log MW vs. elution time for (A) PS standards, polyethoxylated surfactants (B) NPX, (C) tBPX, and (D) APX using a 1000 Å column.

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 Mn 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 weights an average 41 Daltons (34); as a consequence, the Q-factor for the polyethoxylated surfactants is readily calculated using the following equations:

$$M_{\mathrm{aprox}} = (Q/41.4) \times M_{\mathrm{polystirene}} \tag{1}$$

$$\text{Q-factor} \quad \mathrm{NPX} = 41/1.24 = 33.06 \tag{2}$$

$$\text{Q-factor} \quad \mathrm{tBPX} = 41/1.32 = 31.06 \tag{3}$$

$$\text{Q-factor} \quad \mathrm{APX} = 41/1.58 = 25.95 \tag{4}$$

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

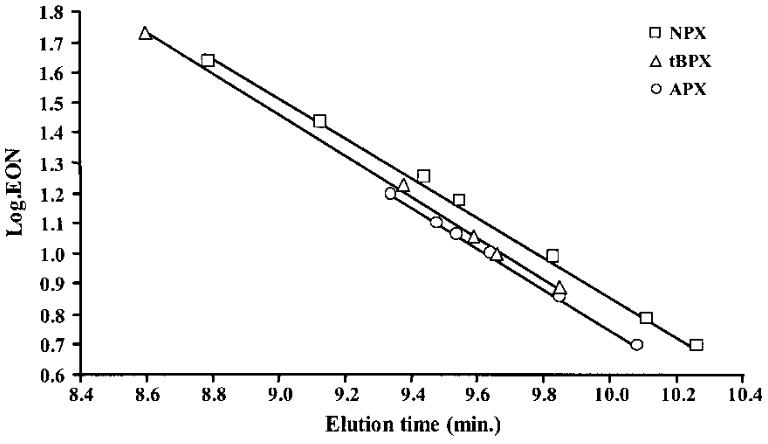

Figure 3. Calibration curve of log EON vs. elution time for NPX, tBPX, and APX using a 1000 Å column.

solution. Furthermore, Fig. 3 shows that the elution time is the average time for the elution of the chemical 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):

$$\overline{\text{EON}} = \Sigma_{\text{i}} \text{ mole fraction ith oligomer} \times \text{i} \qquad (5)$$

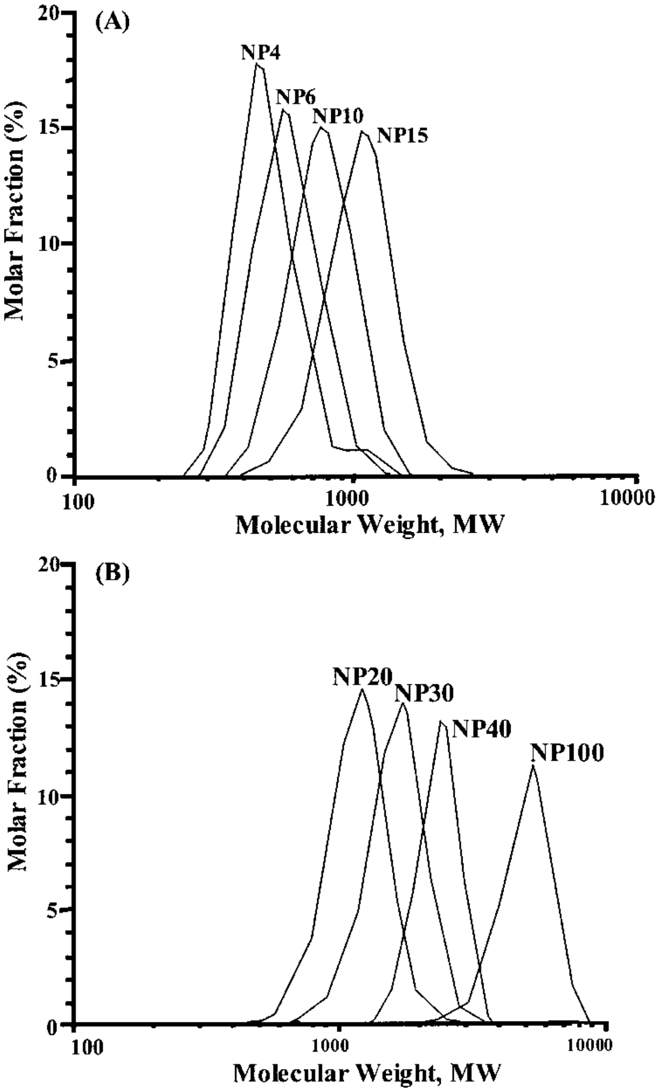

Figure 4. Molecular weight distributions (MWD) of NPX for (A) low etoxylation degree and (B) high etoxylation degree. Conditions as mentioned in Fig. 1.

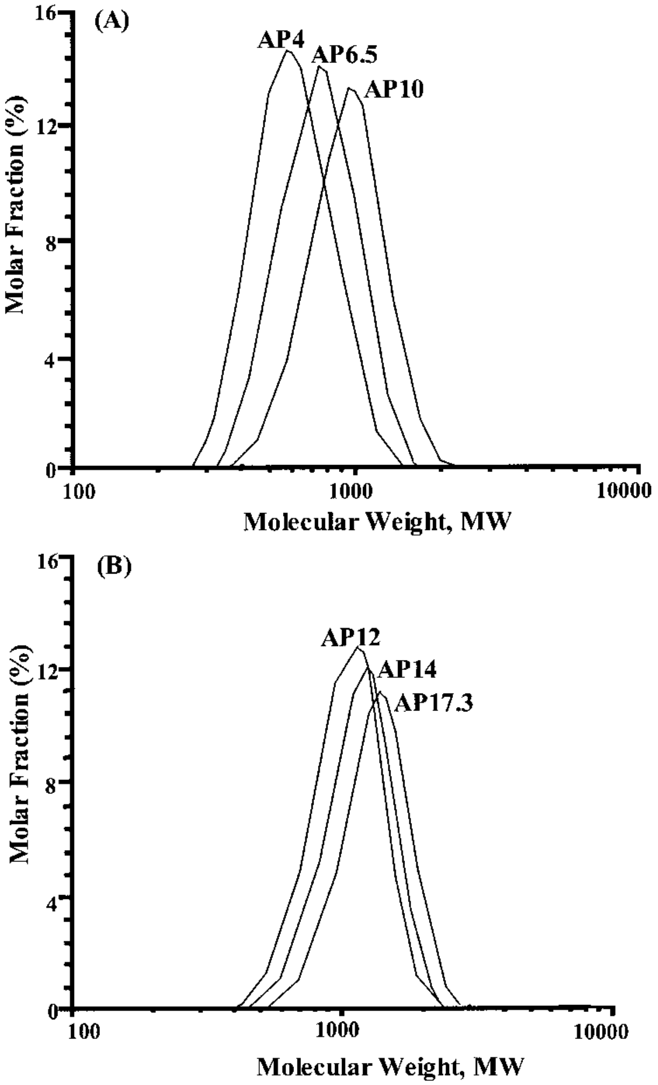

Figure 5. Molecular weight distributions (MWD) of APX for (A) low etoxylation degree and (B) high etoxylation degree. Conditions as mentioned in Fig. 1.

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

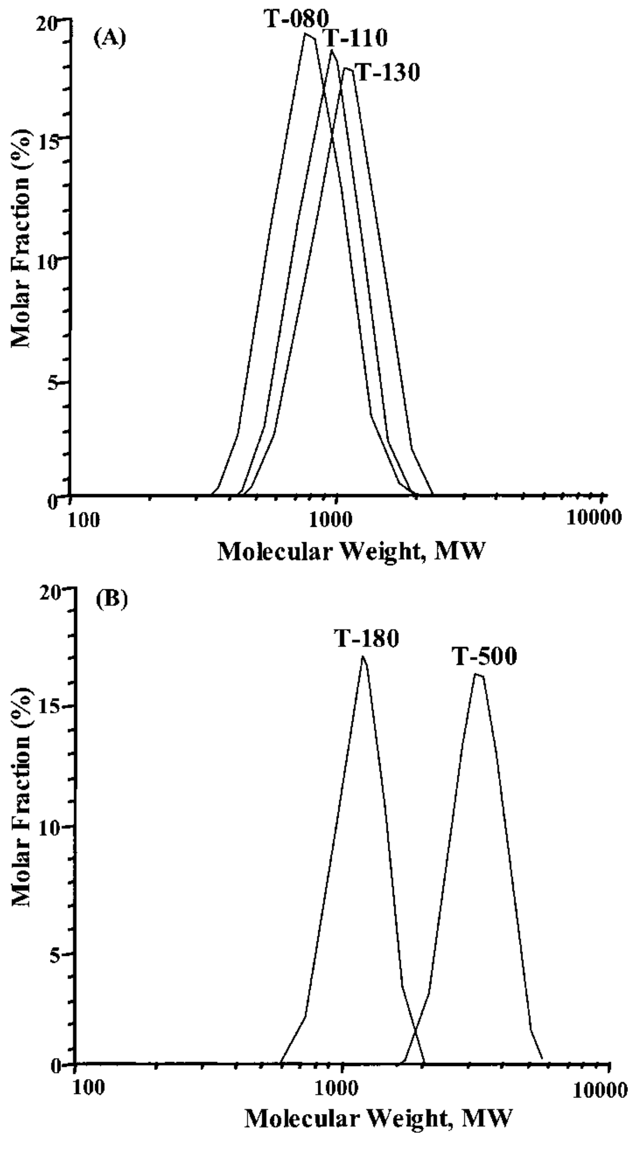

Figure 6. Molecular weight distributions (MWD) of tBPX for (A) low etoxylation degree and (B) high etoxylation degree. Conditions as mentioned in Fig. 1.

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

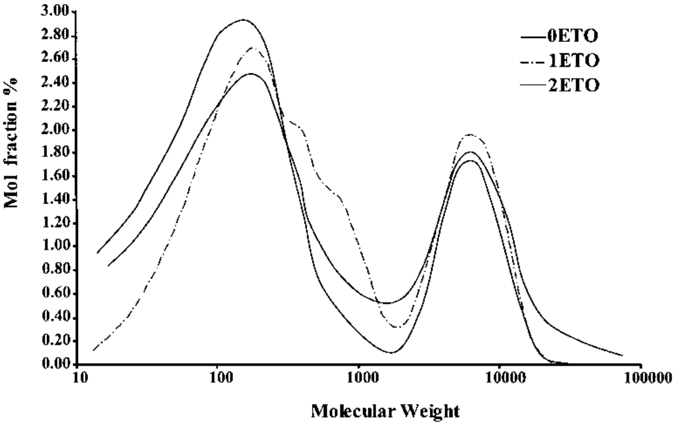

Figure 7. Molecular weight distributions (MWD) of three industrial samples with EON average theoretical 100: (A) 0ETO, (B) 1ETO, and (C) 2ETO. Conditions as mentioned in Fig. 1.

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 0ETO (ethoxylated sample with problem), that is reflected in a bigger EON average and in a the more hydrophilic behavior. In the preparation of asphaltic emulsions the samples 1ETO (ethoxylated sample reference 1, national product) and 2ETO (ethoxylated sample reference 2, 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.

Table 1. HPSEC analysis of polyethoxylated surfactants commercial samples and comparison with HPLC results

	EON$_{\text{AVERAGE}}$					
Sample	HPLC	HPSEC	Theoretical value	MW$_{\text{exp}}$	R.E.%[a]	Mn/MW
Makon 4	4.36	4.40	4	440	9.00	1.06
Makon 6	5.45	6.11	6	489	1.83	1.11
Makon 10	10.80	9.77	10	650	2.30	1.18
Siponic 15	14.55	15.50	15	902	3.33	1.17
Emulgen-920	19.78	18.48	20	1033	7.60	1.25
Emulgen-930	28.48	27.34	30	1423	8.87	1.35
Alkasurf 40	35.70	42.70	40	2099	9.00	1.42
Igepal CO-990	98.70	95.34	100	4415	4.66	1.43
Detex-Ale 4	4.25	4.40	4	399	10.0	1.03
Detex-Ale 6.5	6.85	7.23	6.5	497	6.15	1.05
Detex-Ale 10	9.92	10.02	10	620	0.20	1.10
Detex-Ale 12	11.54	11.55	12	687	3.75	1.11
Detex-Ale 14	13.25	12.55	14	731	10.36	1.11
Detex-Ale 18	18.34	15.59	18	865	9.88	1.19
T-080	6.95	7.95	7	612	13.57	1.10
T-110	10.23	10.66	10	731	6.60	1.11
T-130	11.75	11.82	12	782	1.50	1.13
T-180	17.20	16.64	17	994	2.12	1.20
T-500	47.50	46.70	49	2317	4.69	1.41

[a] Relative error percentage (R.E.%) of EON average obtained by HPSEC with respect to theoretical value.

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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