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Simple High-Performance Liquid Chromatography−Ultraviolet Method To Quantify the Molecular Size Distribution of Nonylphenol Ethoxylates

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ABSTRACT: Polyethoxylated nonylphenols ($NPEO_x$) are widely used in various domestic and industrial applications. These commercial products are mixtures of oligomers that affect aquatic ecosystems, acting as endocrine disruptors. In the present work a simple high-performance liquid chromatography−ultraviolet method to quantify single oligomers of nonylphenol ethoxylates was developed. The following $NPEO_x$ commercial mixtures were analyzed: Igepal CO-520, Igepal CO-630, and Igepal CO-720. Obtained results demonstrate that the absorbance of each oligomer was not a function of the ethoxyl chain length. This result allowed the comparison between experimental molecular distribution functions of $NPEO_x$ mixtures with molecular distributions predicted by the Poisson's equation. In all cases, good agreement was obtained. The method was validated by quantifying $NPEO_x$ samples with different molecular size distributions.

INTRODUCTION

Nonylphenol ethoxylates ($NPEO_x$, where x is the number of ethoxylic units in the molecule) are one of the most used of nonionic surfactants. Technical grade $NPEO_x$ are mixtures of nonylphenols with different lengths of the ethoxylic chain. Products containing $NPEO_x$ are used in many industries, such as textile processing, pulp and paper processing, paints, resins and protective coatings, oil and gas recovery, steel manufacturing, pest control products, and power generation. $NPEO_x$ have also been used in a wide range of consumer products, including cosmetics, cleaners, and paints.[1]

One of the main problems regarding $NPEO_x$ is related to the metabolites produced during its biodegradation. The most common biodegradation pathway of $NPEO_x$ in aerobic bacteria consists of a stepwise removal of the ethylene oxide monomers, producing mono- and diethoxylated nonylphenols ($NPEO_1$ and $NPEO_2$) and nonylphenol (NP) or phenoxy carboxylates.[2−7] These compounds are less soluble in water than the parental molecules, and generally, they are quite recalcitrant to biodegradation and tend to accumulate in aquatic sediments where they can exert toxic effects toward animals and plants. Moreover, short-chain $NPEO_x$ and NP have been included among xeno-estrogens.[8]

$NPEO_x$ can be removed from industrial effluents by several physicochemical or biological methods. Physicochemical technologies include adsorption over activated carbons and polymeric and inorganic adsorbents, ozonation, catalytic and enzymatic peroxide oxidation, and photocatalytic processes. As a general rule, all these treatments are usually complex and expensive; for these reasons, biological methods are preferred.[4−7] In all cases, monitoring the molecular size distribution of $NPEO_x$ is crucial for the evaluation of the treatment process.

Several techniques, such as spectrometry, tensametry, or electrophoresis, are available for the analysis of polyethoxylated surfactants. High-performance liquid chromatography coupled with mass spectrometry (HPLC-MS) has became the most used method because of its broad range of detection, structural identification of the detected molecules, and high sensitivity.[9,10] However, the main disadvantage of this technique is associated with the high cost of the HPLC-MS equipment. In particular, during the identification of the oligomers present in polydisperse samples of $NPEO_x$, it is necessary to use HPLC grade standard of these molecules, which are also very expensive. Thus, there is a need for a convenient and reliable method to determine their concentrations in aqueous samples. For this reason, the objectives of the present work were as follows: (1) to develop a method for a quantitative determination of the individual oligomers in $NPEO_x$ mixtures using high-performance liquid chromatography with UV detection (HPLC-UV); (2) to establish a methodology for the determination of the molecular size distribution of $NPEO_x$ using the developed HPLC-UV method.

EXPERIMENTAL SECTION

Chemicals. Commercial nonylphenol polyethoxylate Igepal (CAS number 68412-54-4) CO-520, CO-630, and CO-720 were from Sigma-Aldrich (Milano, Italy). Other reagents used

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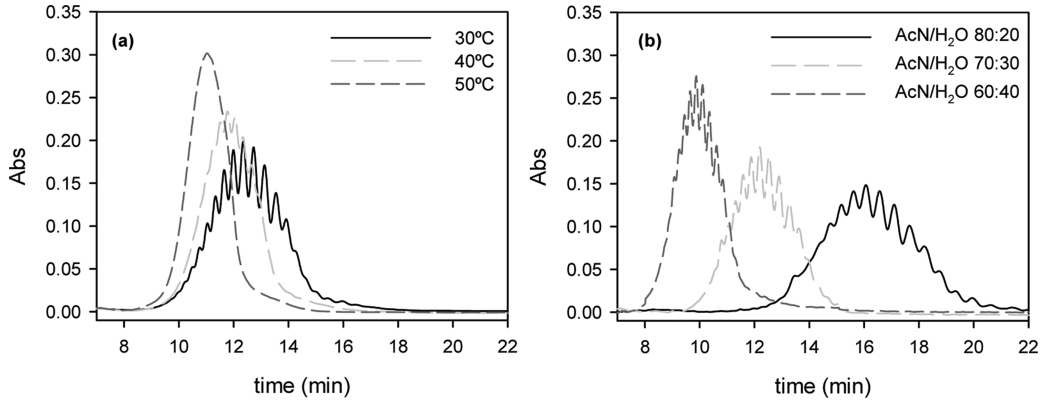

Figure 1. a) Efect of the mobile-phase composition (a) and temperature (b) on the chromatograms corresponding to Igepal CO-630. In panel a the column temperature was 30 °C; in panel b the mobile phase was 70:30 (v/v) AcN/H_2O.

in the present work were HPLC grade. Standard solutions of 1 g L^{-1} Igepal CO-520, CO-630, and CO-720 were prepared as follows. A 100 mg amount of $NPEO_x$ accurately weighed was transferred to a 100 mL volumetric flask and dissolved in a mixture of 50:50 (v/v) acetonitrile/water (AcN/H_2O). Then, these stock solutions were diluted in 50:50 (v/v) AcN/H_2O to obtain the desired concentrations of Igepal.

Instrumentation and Separation Conditions. The HPLC system used in the present work consisted of two pumps (Waters, model 6000A) coupled with a UV−visible diode array detector (Waters, model 2998). When absorption spectra of Igepal samples were performed, wavelengths from 200 to 300 nm (resolution = 1 nm) were used. The oligomers present in the analyzed Igepal solutions were separated using a 5 m Symmestry C_8 column (4.6 mm × 150 mm). In all cases, the injection volume was 50 μL and the flow rate was 0.5 mL/min. With this flow rate, a good compromise between resolution and analysis time was obtained. Mobile phases with different proportions of AcN/H_2O (60:40, 70:30, and 80:20 (v/v)) were tested; in all cases, the isocratic mode was used. The effect of the column temperature on the resolution and on intensity of the chromatographic peaks was also studied; tested temperatures ranged from 30 to 50 °C.

Analysis of the Obtained Chromatograms. Chromatograms were analyzed using the software PeakFit (v. 4.12). This software represents a given chromatogram as the sum of several peaks which are generated by the detected analytes (e.g., the oligomers in a $NPEO_x$ mixture) that are present in the tested sample. The software has a library of functions to represent these peaks; in this work, a Gaussian function was assumed to represent the absorbance corresponding to each individual peak (abs_x):

$$\mathrm{abs}_x = a_0 \exp\left[-\frac{1}{2}\left(\frac{t - a_1}{a_2}\right)^2\right] \quad (1)$$

where a_0, a_1, and a_2 are the amplitude, center, and width of the peak, respectively, and t is time. To analyze a given chromatogram, the software proposes a given number of peaks and calculates the parameters a_0, a_1, and a_2 corresponding to each one. To identify and quantify these single peaks, the second derivative method algorithm was selected from the available library of algorithms of the software. Based on these data, the area (A_x) and the retention time (a_1) corresponding to each individual peak were obtained. In the present work, the parameter a_1 was used to define the retention time of a detected peak. Additionally, the total area (A_T) was obtained by integration over all peaks corresponding to the analyzed NPEO mixture. In all cases, the maximum difference between A_T values of replicate samples was less than 0.02 absorbance units min.

Theoretical Aspects of the Molecular Size Distribution of Oligomers in Commercial $NPEO_x$ Mixtures. Commercial Igepal is produced by the reaction of nonylphenol (NP) with ethylene oxide (EO); the result of this reaction is a mixture of NP with different numbers of added EO molecules ($NPEO_x$) and unreacted NP. Santacesaria et al.[11] demonstrated that for high polimerization degrees, and in agreement with the theory suggested by Flory,[12] the Poisson distribution accurately represents the molecular size distribution of the oligomers in the reaction mixture:

$$\frac{N_x}{N_T} = \frac{e^{-n} n^x}{x!} \quad (2)$$

where N_x is the number of $NPEO_x$ with x molecules of EO added (polimerization degree), N_T is the total number of molecules of $NPEO_x$ (e.g., the summatory over all $NPEO_x$, from $x = 0$ to ∞), and n is the average polimerization degree (e.g., the ratio between reacted EO and N_T).

RESULTS AND DISCUSSION

Effect of the Mobile-Phase Composition and the Column Temperature on the Separation of $NPEO_x$. Figure 1 shows the effect of the mobile-phase composition and the column temperature on the chromatograms corresponding to Igepal CO-630. In all cases, a series of overlapped peaks was obtained. Figure 1a shows that as the percentage of AcN increases, the absorbance at 224 nm decreases and peaks became wider. Because a C8 column was used in this work, it was expected that molecules with higher polarity (e.g., $NPEO_x$ with higher x values) have a lower retention time. When the mobile phase was 60:40 (v/v) AcN/H_2O, a suitable resolution of peaks corresponding to hydrophobic oligomers was obtained. However, peaks corresponding to $NPEO_x$ with large EO added units were overlapped. In order to improve the separation of these peaks, mobile phases with higher proportion of AcN were tested. When a mixture of 80:20 (v/v) AcN/H_2O was used, resolution of the peaks corresponding to low retention time was not suitable. This problem was partially overcame when the composition of the used mobile phase was 70:30 (v/v) AcN/H_2O.

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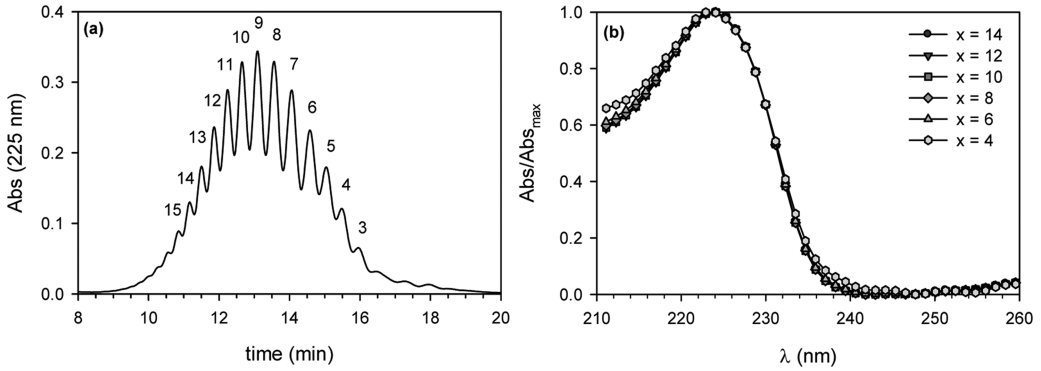

Figure 2. (a) Chromatogram corresponding to Igepal CO-630 and (b) normalized absorption spectra corresponding to the peaks observed in panel a. Numbers indicate the oligomer $NPEO_x$ that was responsible for a single peak.

Figure 1b shows the chromatograms corresponding to Igepal CO-630 obtained at different temperatures using the mobile phase 70:30 (v/v) AcN/H_2O. In general, retention time of the Igepal mixtures decreased as the temperature increased. Because of the lower retention times, separation of peaks was not achieved at temperatures above 55 °C. Although the best results were obtained at 30 °C, lower temperatures could not be tested due to technical limitations. Based on these considerations, all successive chromatographic analysis were performed using a mobile phase of 70:30 (v/v) AcN/H_2O and a column temperature of 30 °C.

Quantification of Total Nonylphenol Polyethoxylate (N_T) and Single Oligomer (N_x) Concentrations in Water Samples. Figure 2a shows that, under the operating conditions selected in the previous section, the chromatograms corresponding to Igepal CO-630 were comprised by several peaks that were partially overlapped. Although the contribution of a given $NPEO_x$ to the total absorbance depends on its concentration (N_x), Figure 2b demonstrates that the normalized absorption spectra corresponding to each peak were similar. This result suggests that the compounds present in each peak are closely related molecules. Moreover, Figure 3 shows that the retention time of a given peak was constant for all of the tested Igepal samples. Assuming that the maximum peak obtained for Igepal CO-630 at time = 13.1 min corresponds to the oligomer $NPEO_x$ with x equal to the average polimerization degree (n = 9, provided by the manufacturer), the other peaks can be easily related with the $NPEO_x$ with different x values. For example, taking into account that a C8 column was used in the present work, $NPEO_x$ with higher x values (e.g., higher polarity) had lower retention times. Thus, the third peak (at t = 11.8 min) before the peak at t = 13.1 min ($NPEO_9$) should correspond to $NPEO_{12}$. Figure 3 shows that the chromatogram of CO-720 exhibited one of the highest peaks at t = 11.8 min. Taking into account that the average polimerization degree corresponding to CO-720 is n = 12 (Table 1) and that, according to eq 2, $NPEO_{12}$ is one of the most abundant oligomers in the CO-720 samples, it can be concluded that one of those highest peaks must correspond to $NPEO_{12}$. This conclusion is in accordance with the above-mentioned assumption that the third peak (at t = 11.8 min) before the peak at t = 13.1 min ($NPEO_9$) should correspond to $NPEO_{12}$. Using a similar procedure, it can be concluded that the fourth peak (at t = 15.1 min) after the peak at t = 13.1 min ($NPEO_9$) must correspond to $NPEO_5$, which is the most abundant oligomer in CO-520 samples. Once again, the chromatogram corresponding to CO-520 exhibited one of the highest peaks at t = 15.1 min (Figure 3).

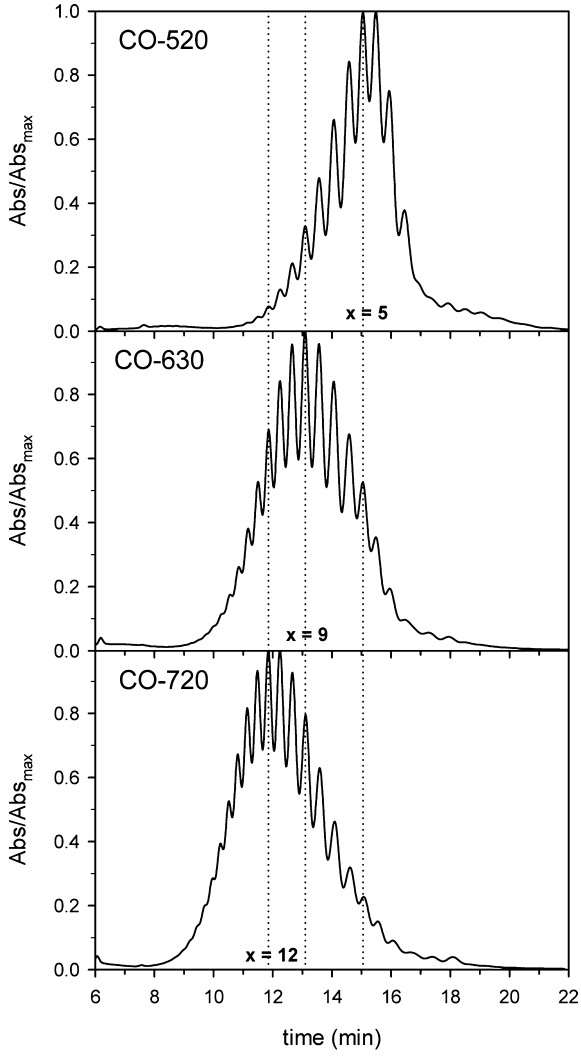

Figure 3. Normalized chromatograms corresponding to Igepal CO-520, CO-630, and CO-720. Dotted lines indicate the retention times corresponding to the maximum absorbances, and numbers indicate the average x value reported by the manufacturer corresponding to each type of Igepal tested.

In order to quantify N_T, calibration curves with standard solutions of Igepal with different concentrations were performed using the conditions selected in the previous

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Table 1. Comparison between the Average Polymerization Degree (n) and the Number Averange Molecular Weight (M_n) Reported by the Manufacturer with the Values Obtained in the Present Work Corresponding to the Tested Igepal Samples

			manufacturer		this work	
sample	Igepal	formula	n	M_n (g/mol)	n	M_n (g/mol)
A	CO-520	$(C_2H_4O)_n{\cdot}C_{15}H_{24}O$	≈5	441	5.35 ± 0.09	455 ± 4
B	CO-630		9−10	617	9.17 ± 0.11	623 ± 5
C	CO-720		10.5−12	749	11.67 ± 0.11	733 ± 5

section. Taking into account the average polimerization degree corresponding to each tested Igepal provided by the manufacturer, according to eq 1, the molecular distribution of $NPEO_x$ in each sample was quite different. However, all of the slopes of calibration curves corresponding to Igepal CO-520, CO-630, and CO-720 were similar (Figure 4), indicating that

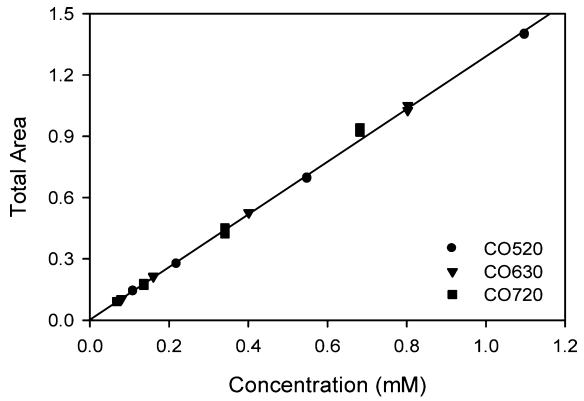

Figure 4. Total area as a function of concentration corresponding to Igepal CO-520, CO-630, and CO-720. In this case, the detection wavelength was 225 nm.

the molar absorptivity of each $NPEO_x$ did not depend on the lengh of the polyethoxyl chain (x). Santacesaria et al.[11] reported that the molar absorptivity of $NPEO_x$ was not dependent on x because the unique aromatic ring present in the oligomers was the responsible for the absorbance.

Figure 4 shows that calibration curves were linear over a factor of 10. The overall linear regression corresponding to A_T as a function of N_T for the tested surfactants yielded a slope s = 1.29 ± 0.01 a.u. min mM^{-1}, y-intercept $y_0 = 2.3 \times 10^{-3} \pm 6.6 \times 10^{-3}$ a.u. min, and a correlation coefficient r^2 = 0.9979 (n = 23 data). The error propagation method was used to calculate the error associated with the quantification of N_T by the proposed technique.[13] Solving N_T from the linear regression, and applying the error propagation method, the following expression was obtained

$$\sigma_N{}^2 = \left(\frac{\sigma_A}{s}\right)^2 + \left(\frac{\sigma_{y_o}}{s}\right)^2 + \left[\frac{(A_T - y_0)\sigma_s}{s^2}\right]^2 \quad (3)$$

where σ_A = 0.01 aumin, $\sigma_{y_o} = 6.6 \times 10^{-3}$ a.u. min, and σ_s = 0.01 au min mM^{-1} are the errors associated with the quantification of the total area, the y-intercept, and the slope, respectively. Considering that the highest concentration tested in the present work was 1.1 mM, this concentration corresponded to a total area of 1.42 a.u. min. Thus, according to eq 3, within the tested Igepal concentrations minimum and maximum errors associated with N_T were $\sigma_{N_{min}}$ = 0.009 and $\sigma_{N_{max}}$ = 0.012 mM. Based on these values, a limit of quantification of 0.045 mM was estimated as the concentration corresponding to five times $\sigma_{N_{min}}$, which corresponded to a maximum relative error of 20%.

Figures 2−4 demonstrate that each peak corresponds to a single $NPEO_x$ and that the molar absorptivity of each $NPEO_x$ does not depend on the number of EO groups (x) bonded to the nonylphenol moiety. Based on these considerations, the following expression can be obtained:

$$\frac{A_x}{A_T} = \frac{N_x}{N_T} \quad (4)$$

where N_x is the concentration of a given $NPEO_x$ in the tested Igepal mixture, N_T is the summatory over all $NPEO_x$ from x = 0−∞, A_x is the area of the chromatogram corresponding to $NPEO_x$, and A_T is the total area. Combining eqs 2 and 4 gives

$$\frac{A_x}{A_T} = \frac{e^{-n}n^x}{x!} \quad (5)$$

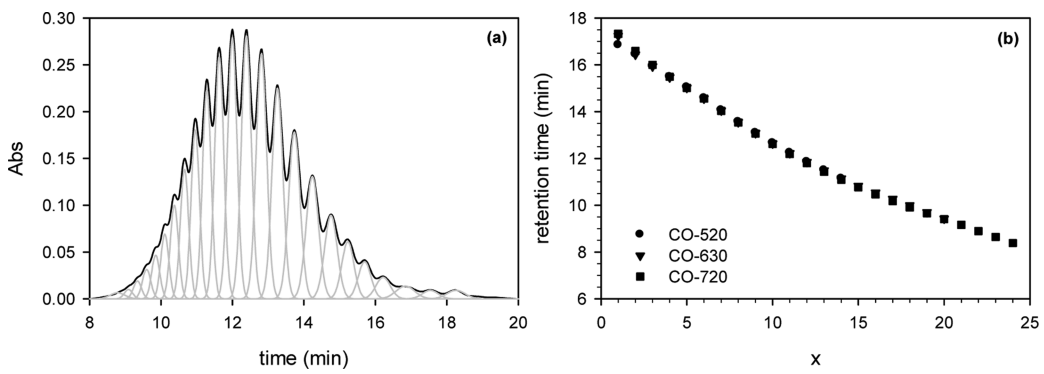

Figure 5. (a) Example of the fitting procedure to evaluate the area of each $NPEO_x$ (A_x). The black line represents the chromatogram corresponding to CO-720; gray lines denote the individual peaks obtained by the fitting procedure. (b) Retention time of each individual peak (a_1, eq 5) as a function of the polimerization degree (x) of the $NPEO_x$ present in Igepal CO-520, CO-630, and CO-720 samples.

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Equation 5 shows that if the molar absorptivity of each $NPEO_x$ does not depend on x, the ratio A_x/A_T must follow the Poisson distribution. The software PeakFit (v. 4.12) was used to evaluate the area of each $NPEO_x$ (A_x) and the total area (A_T). Figure 5a shows that the selected fitting procedure could adequately identify the individual peaks corresponding to each $NPEO_x$ in the analyzed Igepal samples. Taking into account the relative time positions of the single peaks corresponding to Igepal CO-520, CO-630, and CO-720 (Figure 3), the retention time of each individual $NPEO_x$ was obtained. Figure 5b shows that the retention time (a_1, eq 5) of a given oligomer $NPEO_x$ was constant and it does not depend on the tested Igepal sample; moreover, the width parameter corresponding to each detected peak (a_2, eq 5) was also constant (a_2 = 0.14 ± 0.01 min). These results confirm that each peak corresponded to a single $NPEO_x$ with a definite x value.

Molecular size distributions corresponding to Igepal CO-520, CO-630, and CO-720 were obtained as follows. For each Igepal sample, a_1, A_x corresponding to the single peaks that comprised the whole chromatogram (Figure 5a), and A_T were obtained using the software PeakFit. Because the retention time corresponding to each $NPEO_x$ was known (Figure 5b), the fraction of each $NPEO_x$ was calculated as the ratio A_x/A_T (eq 4).

Figure 6 shows that the obtained molecular size distributions corresponding to the tested Igepal samples were asymmetric

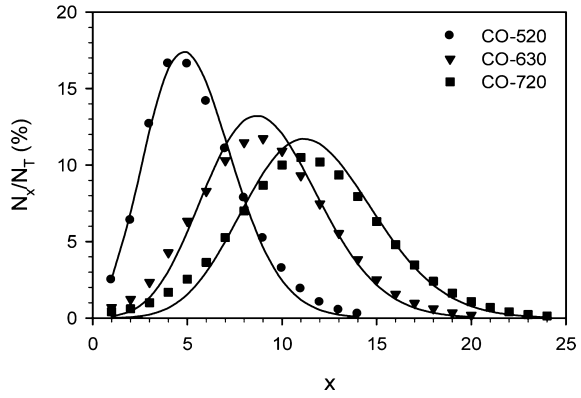

Figure 6. Experimental molecular size distribution of the tested Igepal samples. Lines indicate the results obtained by fitting eq 5 to the experimental data; results are depicted in Table 1.

bell-shaped curves, in accordance with the Poisson distribution. Equation 5 was fitted to the experimental molecular distribution of each Igepal sample to obtain n. Table 1 shows that both n and M_n corresponding to all the tested Igepal samples obtained in the present work were similar to those reported by the manufacturer, providing a strong validation of the proposed technique to evaluate the molecular distribution of $NPEO_x$ in Igepal samples.

Using the Developed HPLC Technique to Analyze Igepal Mixtures of Unknown Molecular Size Distributions. The HPLC technique described above was used to analyze Igepal mixtures with other molecular size distributions rather than the Poisson distribution. Stock solutions with 500 mg/L of CO-520, CO-630, and CO-720 were prepared in 50:50 (v/v) AcN/H_2O. These stock solutions were mixed in different known proportions to obtain a $NPEO_x$ molecular size distribution that was a combination of two Poisson distributions. Then, stock solutions and prepared mixtures were analyzed by HPLC to obtain the total concentration of $NPEO_x$ (N_T), and the $NPEO_x$ distribution function as it was described in the previous section.

Figure 7 (left panel) shows several examples of chromatograms corresponding to the prepared Igepal mixtures. As it was previously obtained for the original IgepaI samples (Figure 3), its mixtures also produced chromatograms composed by overlapped peaks. Table 2 shows that the proposed HPLC method could adequately quantify the total $NPEO_x$ in both original Igepal samples (Table 2, samples A−C) and prepared Igepal mixtures (Table 2, samples D−H); in all cases, the absolute error was less than 5% of the actual N_T concentration.

Figure 7 (right panel) shows the experimental molecular size distribution of $NPEO_x$ in the mixtures D, F, and H (Table 2) determined by the proposed HPLC method. Although the shape of the molecular size distribution in mixtures D and F were similar to a Poisson distribution, the experimental distribution corresponding to the mixture H clearly exhibited a shoulder. In order to verify if this shoulder corresponded to the actual distribution or if it was an experimental artifact, the molecular size distribution of $NPEO_x$ in these mixtures was calculated as follows. First, it was assumed that the molecular size distribution of $NPEO_x$ in the original Igepal solutions corresponds to the Poisson's distribution. Then, if n and N_T corresponding to each stock solution (A−C, in Table 2) are known, the molecular distribution of $NPEO_x$ in a given mixture was calculated using the following expression

$$\frac{N_x}{N_T} = \frac{\left(\frac{e^{-n_A} n_A^{\,x}}{x!}\right) f_A N_{TA} + \left(\frac{e^{-n_B} n_B^{\,x}}{x!}\right) f_B N_{TB} + \left(\frac{e^{-n_C} n_C^{\,x}}{x!}\right) f_C N_{TC}}{f_A N_{TA} + f_B N_{TB} + f_C N_{TC}} \quad (6)$$

where f_A, f_B, and f_C are the volume fractions of the stock solutions A, B, and C in the mixture. Equation 6 was used to calculate the molecular size distribution of $NPEO_x$ corresponding to mixtures D, F, and H (Table 2) using the experimental n values depicted in Table 1 corresponding to the original commercial samples (A, B, C). Figure 7 (right panel) shows that the molecular size distributions obtained by the proposed HPLC-UV method agree with those calculated using eq 6. This result demonstrates that the HPLC-UV method developed in the present work can be useful in analyzing Igepal samples with unknown distributions of $NPEO_x$. This method could be particularly useful in the study of the aerobic biodegradation of Igepal in water samples, for example.

CONCLUSION

In this work, a simple HPLC-UV method for the quantitative determination of the oligomers present in water samples of $NPEO_x$ was developed. The method comprises a partial separation of the oligomers using a reversed phase C8 column, mobile phase 70:30 (v/v) AcN/H_2O under isocratic mode operated at 30 °C. Although the obtained chromatograms consisted of several overlapped peaks, the software PeakFit allowed obtaining the contribution of each peak to the total absorbance. Obtained results demonstrate that (1) each peak represents a $NPEO_x$ with a definite degree of condensation (x); (2) the molar absorptivity of each $NPEO_x$ does not depend on x; (3) the obtained molecular size distributions corresponding to the tested commercial mixture samples were in accordance with the Poisson distribution; (4) both the average polimerization degree (n) and the average molecular weight

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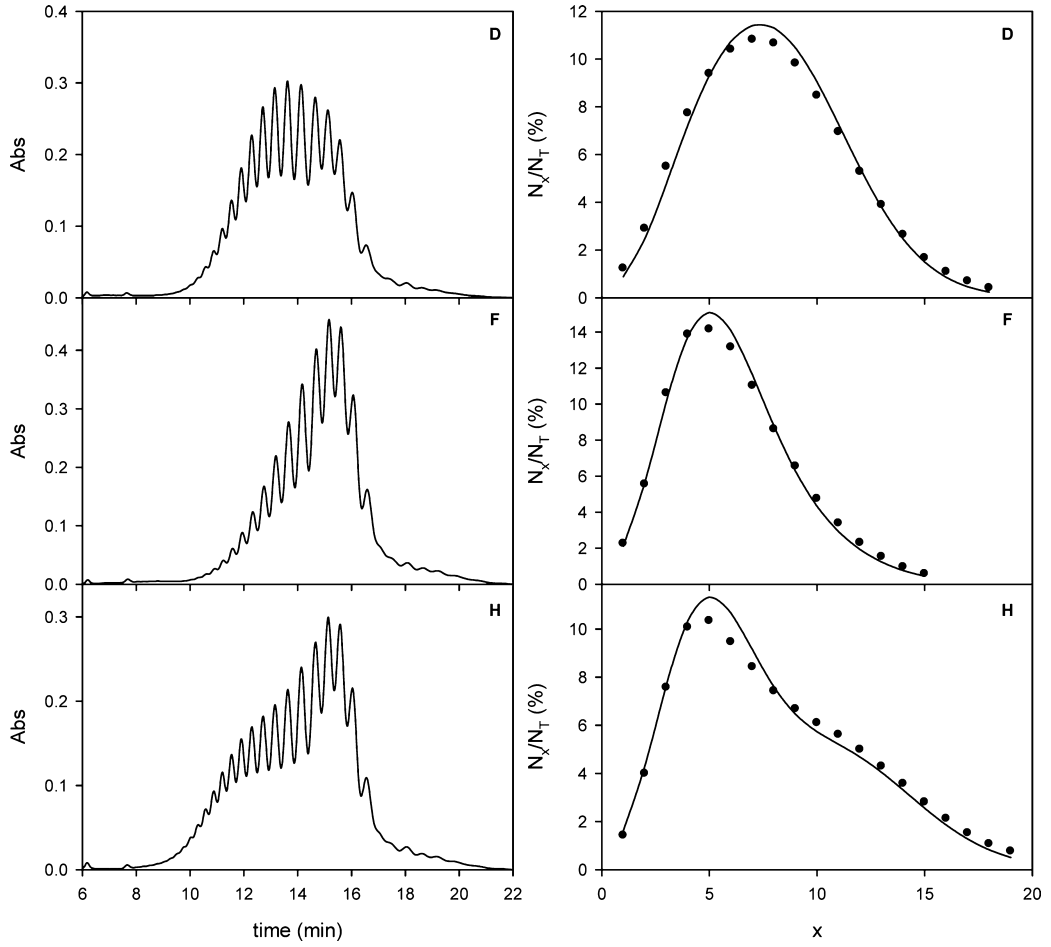

Figure 7. Chromatograms (left panel) and molecular size distributions (right panel) corresponding to the mixtures D, F, and H (see Table 2). Lines indicate the molecular distribution calculated using eq 6 considering the average polimerization degree (n) of the original Igepal samples (A–C) obtained in the present work (see Table 1).

Table 2. Results of HPLC Analysis of the Original Igepal Samples (A–C), and Igepal Mixtures with Other Molecular Size Distribution Rather Than the Poisson Distribution (D–H)

	volume fraction (f)					
sample	CO-520	CO-630	CO-720	N_T (mM)	N_T (mM) (by HPLC)	error (%)
A	1	0	0	1.10	1.09	−1.3
B	0	1	0	0.80	0.81	0.8
C	0	0	1	0.68	0.71	4.6
D	0.25	0.75	0	0.88	0.88	0.0
E	0.50	0.50	0	0.95	0.97	2.0
F	0.75	0.25	0	1.03	1.02	−0.2
G	0	0.50	0.50	0.74	0.77	3.7
H	0.50	0	0.50	0.89	0.89	0.0

corresponding to all of the tested $NPEO_x$ samples obtained in the present work were similar to those reported by the manufacturer; (5) using the proposed HPLC-UV method, the error corresponding to the total $NPEO_x$ concentration (N_T) in original Igepal samples, and in prepared mixtures was less than 5% of the actual N_T concentration; and (6) the molecular size distribution of mixtures of commercial Igepal samples with other distributions rather than the Poisson function were obtained using the HPLC-UV method developed in the present work.

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Notes

The authors declare no competing financial interest.

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