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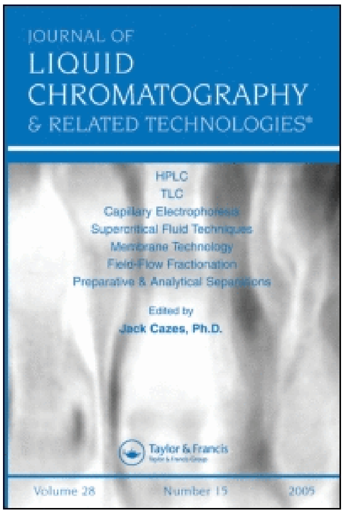

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ANALYSIS OF ETHOXYLATED NONYLPHENOL SURFACTANTS BY HIGH PERFORMANCE SIZE EXCLUSION CHROMATOGRAPHY (HPSEC)

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ABSTRACT

Since Size Exclusion Chromatography does not provide a complete oligomer resolution, it has not been generally considered as a choice method for analyzing ethoxylated surfactant.

However, this situation might be changing. In effect, the use of new column technology together with non aqueous carrier solvent, and some operational optimization, can result in fairly good distribution data on the number of ethylene oxide groups per molecule (EON).

It is shown that HPSEC provides an excellent EON average estimate over a wider and higher EON range than the the up-to-date HPLC techniques.

INTRODUCTION

Size Exclusion Chromatography (SEC) has been proposed in several instances in the past 30 years as a method to characterize nonoionic surfactants (1-3). However it seems that all trials ended in a failure to attain reliable data, and that the results were good only to provide a qualitative comparison between two substances.

The main problem in analyzing surfactants by SEC seems to come from the formation of micelles in water and other solvents. A micelle is a kind of aggregation polymer that occurs as soon as a certain concentration, so-called Critical Micellar Concentration (CMC) is reached. As a matter of fact some authors have proposed to use a early version of SEC, so-called Gel Permeation Chromatography (GPC) to estimate the extent of micelle formation (4). Naguschi reported extensive studies on the separation of nonionic surfactant species on polyvinyl alcohol columns with acetonitrile/water mixture as the mobile phase (5). He found that the lower the degree of ethoxylation was, the higher was the percentage of acetonitrile required to elute the compound; additionally, there was some evidence that the separation was not due entirely to size exclusion effects.

Recent technological advances have placed on the market new column packings made of very small spherical particles in the 3-5 µm range versus the 30-50 µm size available a few years ago. It is now possible to use SEC to analyze compounds with molecular weight in the range of a few hundred daltons (6). Moreover, the increased sensitivity of the new detection devices allows to dilute the solutions below the CMC, or to detect all molecules associated into micelles whenever aggregation occurs (7-10).

Recent publications on HPLC analysis have reported that the ethoxylated alkylphenol surfactant oligomers can be readily detected by UV absorbance or fluorescence techniques (11-12). Although it is generally less sensitive, the refractive index detection can be quite useful too, since it has be found (13) to correlate with both the surfactant concentration and the number of ethylene oxide groups per molecule so-called EON. It is worth noting that it can be used advantageously with compounds that do not absorb in the near UV or Vis spectra.

The EON distribution of ethoxylated nonionic surfactants has been extensively reported in the literature. As mentionned by Shick (2) more than 25 years ago, the EON distribution is usually of the Poisson type, according to the polycondensation mechanism of the reaction of ethylene oxide addition in alkaline medium. Unless they are mixed, very few commercial products with short EO chain depart significantly from the Poisson distribution (14); as will be seen later on, it is not the case of long EO chain surfactants.

Because of their widespread Poisson distribution, commercial ethoxylated nonionic surfactants can often contain substances that are very oil-soluble, as well as others that are very water-soluble. If an oil-water two-phase system is available, then the different surfactant species can behave independently from one another, and the result can be a severe fractionnation, in which the actually active surfactant mixture at interface is considerably different from the overall surfactant composition. Fractionnation has been recently investigated, and a satisfactory modeling has been proposed (15-16). The model makes use of fractionnation data, which require in turn the analysis of every oligomer in all phases. Column chromatography and thin layer chromatography techniques have been reported (17-19); however, they were not found appropriate for routines work, nor for analyzing nonionic surfactants containing long EO chains.

Very recently, HPLC techniques to analyze ethoxylated nonylphenol mixtures were enhanced to the point, where oligomers from 1 to 40 EON could be separated in a single run (20-22). This was quite an improvement; nevertheless, even higher EON oligomers are often required in wetting, detergency and foaming applications (23). Since surfactants with EON in the 50-100 range can be considered as small macromolecules, a HPSEC approach was selected in the present paper to address this problem.

FACTORS INFLUENCING THE HPSEC

Three factors should be considered in order to master the SEC technique: (1) the solvent nature and effect, (2) the efficiency of the column or column set, (3) the calibration and resolution of the column.

The selection of the eluting fluid in SEC is not critical, provided that it is a strong enough solvent, so that no other mechanism can happen, but size exclusion. As far as ethoxylated nonylphenols are concerned, the are soluble in short chain alcohol (< C5), chloroform and tetrahydrofurane (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 this latter is the selected solvent. When used as the mobil phase in SEC, THF is known to exhibit in most cases the so-called "differential solvation" (6) effect.

The two other factors, i.e., efficiency (N) and resolution (R), which are traditionally handled in other chromatographic techniques by a test with monomeric substances, cannot be dealt with the same way in SEC.

Yau and collaborators (24) introduced recently the "specific resolution" (Rsp) to free the resolution concept from the influence of the calibration sample nature in the linear range of response.

$$Rsp = \frac{0.576}{(\sigma D_2)} \qquad [1]$$

D_2 is the slope of the linear response range of the calibration curve, σ is the standard deviation, which is related to the number of theoretical plates in the case of a given substance, and can be estimated easily by (25):

$$\sigma = \frac{W}{(2\sqrt{2\pi})} \qquad [2]$$

where W = the peak width at the base.

In order to compare columns, equation [1] should be referred to a standard column length (L):

$$Rsp^* = \frac{0.576}{(\sigma D_2\sqrt{L})} \qquad [3]$$

Yau and col. established that the relative error between the true and experimentally determined molecular weights, i.e., a critical parameter for evaluating the method, is given by:

$$M^* = e^{\frac{1}{2}(\sigma D2)} - 1 \qquad [4]$$

From these expressions, it is seen that the resolution is maximized, and the error minimized, whenever the σ D_2 group is minimum. As a consequence both parameters must be evaluated in the column selection process.

APPARATUS AND EXPERIMENTAL PROCEDURES

Several Perkin-Elmer HPLC modules were used in the equipment setting: a LC-250 pump, a LC-OVEN 101 thermostated enclosure and a LC-30 refractive index detector. The injector was a Rheodyne 7125 model with a 10 µl loop. The data was handled through a DTK personal computer with a PE Nelson 900 series interface and a SEC software version 5.1.

In preliminary trials a ZORBAX PSM 60S column was tested with no satisfactory results. Two other columns were used : (1) A PLgel 5 µ mixed-C column (30 cm x 7.5 mm) from Polymer Laboratories with a MW range from 10^3 to 10^7. This column is referred to as the linear column in the following text because it is filled by linear mixed beads of differents pores sizes (10^3 - 10^6 Å). (2) A Ultrastyragel 100 Å column from Waters, made from crosslinked styrene-divynil benzene gels with a low MW range from 100 to 1000 (30 cm x 7.8. mm I.D.). This column is referred to as 100 Å column in the following text.

Tetrahydrofurane (THF) HPLC grade from Baker Chemicals was used as the carrier solvent. Pretreatment of the solvent included: (1) filtration on a non-aqueous 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.

Two polystyrene standard sets from Polymer Laboratories were used: (1) a medium weight P/N 2010-0100 sample with MW ranging from 580 to 3.15 10^6, and (2) a low molecular weight P/N 2010-0101 sample with MW ranging from 162 to 22000. Each standard set contains 10 calibration samples and a verification sample. Verification samples exhibit MW of 580 and 1700 daltons respectively. A pure non-ethoxylated nonylphenol from Aldrich was also used as a reference.

Commercially ethoxylated nonylphenol surfactants from various manufacturers were tested: Makon M series from Stepan Chemicals, Igepal

CO series from Gaf Chemicals, Siponic NP series from Alcolac, Carsonon N series from Carson Chemicals, Alkasurf NP series from Alkaryl Chemicals, Emulgen E9XX series from Kao Atlas Japan, and Arkopal NP from Hoechst GmbH. In the following text, these susbtances are referred to as NPX or Trade-NameX, where X stands for the average number of ethylene oxide groups (EON) per nonylphenol molecule.

A UV detector was tested at the wavelengths corresponding to both absorbance maxima in THF (233 nm and 275 nm), but the response was not found satisfactory, probably because of the low concentration level (0.2 wt.%) required to avoid the formation of micelles. Thus, a refractive index detector was used instead, this time with reliable results.

HPSEC experiments were carried out in the following conditions, unless otherwise stated: temperature 40 ºC, flow rate 1 ml/min and refractive index at 8x. The efficiency and resolution were computed according to equations [2] to [4].

RESULTS AND DISCUSSION - MW CALIBRATION RUNS

First, the linear column was used alone, and calibration runs were carried out with the low MW polystyrene standards. Fig. 1-A indicates the relationship between the standards' molecualar weight and the elution time. The variation of the logarithm of the molecular weight versus the elution time is obviously linear, with an excellent correlation coefficient. The two black points indicate the position of the verification standards (at 1700 and 580 daltons). The higher molecular weight standard is exactly in line, whereas the lower molecular weight one is slightly shifted below the line, an indication that the efficiency decreases in the lower MW range. This is no surprise since the column specification minimum MW is 1000 daltons.

Different commercial nonylphenol ethoxylates from the Igepal CO and Arkopal NP families are analyzed according to the same procedure. Since these substances 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. Fig 1-A shows the molecular weight vs elution time graph for nonylphenol ethoxylates ranging from EON= 9 to EON = 85. It is worth remarking that

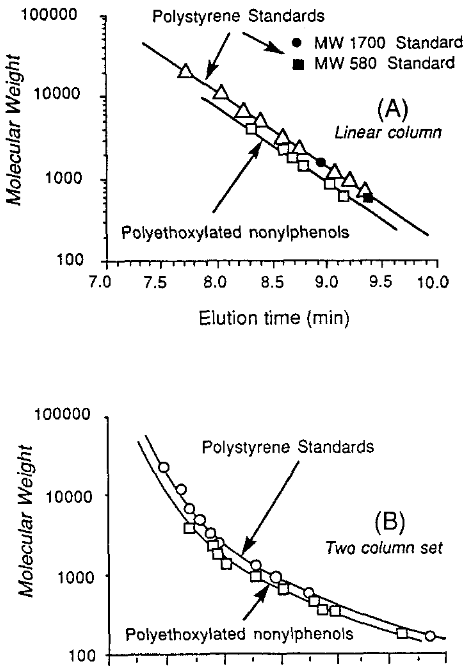

FIGURE 1. Calibration curves. (A) PLgel linear column. (B) Two column (linear +100 Å) set.

the log MW versus time graph exhibits an excellent linearity, a feature suitable for a calibration curve. Moreover, the line slope is exactly the same as in the polystyrene standards calibration graph. This shift is surely due to differences in the relationship between the molecular weight and the hydrodynamic volume. In effect, the polystyrene macromolecule has probably a larger gyration radius (and also larger hydrodynamic volume) than the corresponding ethoxylated nonylphenol molecule, because the polyethylene oxide chain is known to fold on itself to form a ball. Extra molecular weight is also conferred by the presence of oxygen atoms.

The parallelism of the two lines in a logarithmic scale, means that there is a constant factor between the two results. Thus for a given elution time, the ethoxylated nonylphenol molecular weight can be deduced readily from the corresponding polystyrene molecular weight by dividing by 1.50, all over the range.

It is known that for each Å in length, a polystyrene molecule weights 41 daltons in average (26); as aconsequence the Q-factor for the NPX substances is readily calculated as:

$$\text{Q-factor}_{NPX} = 41/1.5 = 27 \qquad [5]$$

This value allows the calculation of the average MW of a NPX sample from the MW of the polystyrene specie with the same elution time.

It is of course even easier to use the NPX straight line in Fig. 1-A as a calibration curve for this type of substance.

As a way to evaluate better the performance of this column, the different efficiency parameters (σ, σD_2, Rsp* y M*) are calculated from the chromatograms of the Igepal CO family. The results are shown in Table 1. Whenever Rsp* is larger than 1, there is a good resolution between substances with molecular weights differing by less than MW/10. According to Table 1 results, this is occuring for oligomers with molecular weight greater than 750, i.e. for EON > 12. This is consistent with the previous remark on the lower limit of the linear column according to the polystyrene data.

In order to enhance the resolution in the low molecular range, a 100Å column is added in series to the linear column. Lower MW samples are tested, i.e., MW=162 polystyrene and NP6, NP4 surfactants. Fig. 1-B shows the resulting data in the same fashion as in Fig. 1-A. As previously there is a correlation (as a multiplicative factor) between the MW of the polysterene and the ethoxylated surfactant, which is here 1.55, a value very similar to the previous one.

This means again that polystyrene can be safely used as a standard for the determination of the MW of the surfactants, provided that the multiplicative factor is applied for correction purposes.

Table 1 indicates the performance data for the two-column set. The lower limit (Rsp* $\geq$ 1) is shifted down to EON=8 or MW=500. Since MW/10 is 50 daltons and since an ethylene oxide unit weights 44 daltons, it may be stated that the resolution at the low EON limit is almost 1 EON unit, a performance that almost matches HPLC separation. As far as the error (M*) is concerned, it is clear that the two-column set enhances the accuracy on the MW estimate, particularly at the low EON limit.

TABLE 1. Efficiency parameters calculated for the linear column and the two column (linear + 100Å) set.

Sample	EON average	(σD2)		(Rsp*)		(M*)	
		Linear Column	Two column set	Linear Column	Two column set	Linear Column	Two column set
Igepal 990	85.5	0.071	0.049	1.48	1.52	0.3	0.1
Igepal 970	45.5	0.080	0.051	1.31	1.46	0.3	0.1
Igepal 890	36.4	0.089	0.051	1.18	1.46	0.4	0.1
Igepal 880	27.6	0.106	0.054	0.99	1.38	0.6	0.2
Igepal 850	18.0	0.106	0.063	0.99	1.18	0.6	0.2
Igepal 730	13.5	0.106	0.063	0.99	1.18	0.6	0.2
Igepal 720	11.0	0.124	0.073	0.85	1.02	0.8	0.3
Igepal 660	8.7	0.124	0.073	0.85	1.02	0.8	0.3
Arkopal NP6	6.0	---	0.102	---	0.73	---	0.5
Igepal 430	4.0	---	0.122	---	0.61	---	0.8
Nonylphenol	0.0	---	0.141	---	0.53	---	1.0

RESULTS AND DISCUSSION - EON CALIBRATION RUNS

In most cases the result of interest is more the average number of ethylene oxide groups per surfactant molecule, than the molecular weight. Then, the calibration curves are plotted as the logarithm of EON versus the elution time. Fig. 2 indicates an excellent correlation from EON = 10 to 85 with the linear column, and from EON = 4 to 85 with the two columns in series. In the first case the plot is linear, which is not surprising since the MW and EON varies essentially in the same fashion.

Note that in these data, the elution time is the average time for the chromatogram peak to get out and the EON is the average value for the commercial sample. The EON average value ($\overline{EON}$) is calculated by means of a linear mixing rule based on the mole fractions (14,22):

$$\overline{EON} = \sum_{i} \text{mole fraction } i^{th} \text{ oligomer} \times i \qquad [6]$$

It is known that this average matches the physicochemical average. In any case it is very close to the distribution mode, particulary for high EON values.

Fig 3-A shows the chromatograms resulting from the HPSEC analysis of a NP4 sample with the two columns in series. The black dots indicate the actual RI detector output, i.e., the experimental HPSEC

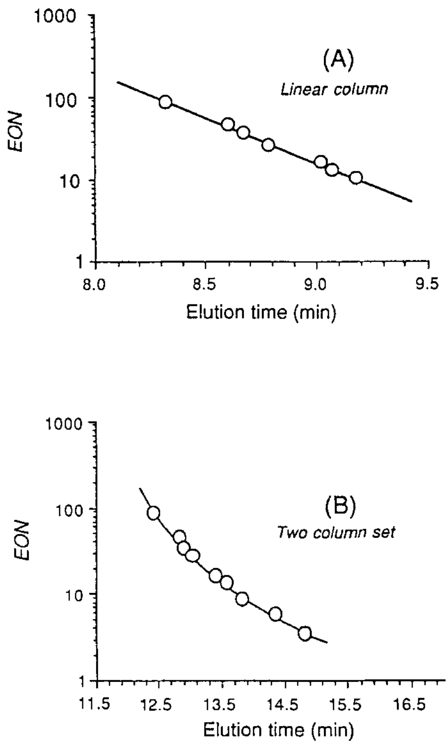

FIG. 2 : Calibration curves EON vs. Elution time.
(A) Plgel linear column. (B) Two column (linear plus 100 Å) set.

distribution, while the white dots indicates the Poisson distribution with the same EON average, and the solid line refers to the HPLC data according to a method reported elsewhere (14).

It is seen that the NP4 chromatograms are in good agreement, and that the Poisson distribution model is quite satisfactory for this case. It can be said that HPSEC gives an excellent estimate of both the distribution and the average value. Note also that the maxima are in good coincidence. The slight difference between the HPSEC and HPLC chromatograms is probably due to the fact that the HPLC method does not detect higher oligomers as well as low EON ones. As a consequence the fraction of low EON oligomers is often overestimated.

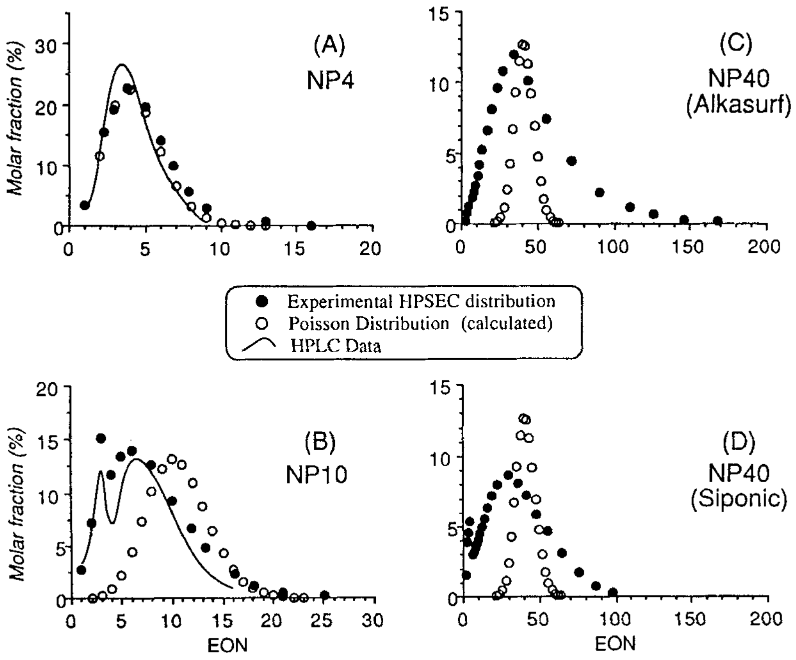

FIG. 3 : Comparison of calculated and experimental EON distributions for samples: (A) Makon 4, (B) Makon 10, (C) Alkasurf 40 and (D) Siponic 40. Conditions: as mentioned with two column set.

The NP10 data (Fig. 3-B) indicate that the HPSEC ouput and HPLC ouput are in agreement. On the contrary, it is clear that the Poisson distribution is not a satisfactory model, as pointed out by Nadeau (27).

Fig. 3 C and D indicate the HPSEC and Poisson distribution models for two NP40 samples. In both cases the HPSEC data allow to calculate the correct average EON, i.e. EON= 38.8 and 32.6 respectively, which is the important feature, as far as the performance of the method is concerned. On the other hand, it is evident that the experimental chromatograms exhibit a much wider distribution than the Poisson model. Note that the Alkasurf 40 sample is even more widely distributed then the Siponic 40 sample, although this latter presents a secondary peak at low EON, a characteristic already seen in Makon 10 (Fig. 3-B), that reduces the current

TABLE 2. HPSEC analysis of commercials samples and comparison with HPLC results.

Sample		EON average		Mn	Mw	$D = \frac{Mw}{Mn}$
		HPLC	HPSEC			
NP4 MW=396	Makon 4	4.0	4.1	359	383	1.07
	Carsonon4	-	4.9	388	413	1.06
	Alkasurf 4	-	4.1	355	378	1.06
NP6 MW=484	Makon 6	5.2	5.1	376	415	1.10
	Alkasurf 6	-	5.8	404	452	1.12
NP8 MW=572	Makon 8	7.0	6.9	441	500	1.13
	Carsonon 8	-	7.2	453	516	1.14
	Alkasurf 8	-	6.6	431	492	1.14
NP9 MW = 616	Siponic 9	-	7.5	453	529	1.17
NP10 MW = 660	Makon 10	7.3	7.2	447	517	1.16
NP30 MW=1540	Carsonon 30	-	25.3	795	1317	1.66
NP35 MW=1760	Emulgen 935	-	32.0	1212	1622	1.34
NP40 MW=1980	Siponic 40	-	32.6	967	1650	1.71
	Alkasurf 40	39.2	38.8	1323	1927	1.46

EON average by several units. As a matter of fact this multimode distribution is probably an evidence of some mixing in the manufacturing process.

EVALUATION OF THE HPSEC METHOD

The previous sections indicate that the HPSEC method with two columns in series leads to satisfactory estimates of the average EON of nonylphenol ethoxylates. The method was applied to a variety of samples produced by different manufacturers, and the results were gathered in Table 2. The average EON value computed from HPSEC data matches pretty well the manufacturer estimate and the available HPLC data(14,20,21). The calculated molecular weights are also in good agreement with other reliable informations, say within a 10% error in most cases. However, discrepancies up to 20% are observed with products exhibiting a bimodal distribution (Siponic 9 & 40, Makon 10, and Carsonon 30 samples). Table 2 also reports the data dispersion, i. e., the ratio of the weight and number means (D = Mw/Mn). The computed values ranges from 1.0 to 1.4, as expected from the synthesis mechanism. Exceptions are found for the products that exhibit a bimodal distribution and are obviously the result of some mixing.

At the light of recent reports on the HPLC analysis of nonylphenol ethoxylates (14,20,21), HPSEC is found to exhibit interesting features. Although it does not match the single oligomer separation attained by gradient mode HPLC up to EON=25, it has several advantages over HPLC techniques. First, it requires less expensive equipments, particularly because of the isocratic mode and RI detector; then, it gives fairly good results as far as the average EON is concerned; finally, it provides the best estimate for highly ethoxylated substances, with no theoretical limit but the solubility in THF, whereas currently available HPLC methods do not reach beyond EON=25.

CONCLUSIONS

The reported results show that HPSEC techniques are worthwhile to analyze etholylated nonylphenol surfactants. Provided that two columns are used in series, a good average EON estimate can be attained over an extremely wide range of molecular weight. For surfactants with more than 30 ethylene oxide groups per molecule, HPSEC seems to be the choice method, since it is both more performant and less expensive than the competing HPLC techniques.

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