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Note

High-performance liquid chromatographic method for determining ethoxymer distribution of alkylphenoxy polyoxyethylene surfactants

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Non-ionic polyethoxylated surfactants, although widely used for many years, have had few characterization techniques capable of defining their wide range of ethoxymer distributions.

Using circular thin-layer chromatography, Konishi and Yamaguchi[1] showed that a nonylphenoxy polyoxyethylene ethanol of average ethylene oxide (EO) number $n = 9$ generally followed a Poisson distribution. Nadeau *et al.*[2], examined nonylphenoxy polyoxyethylene (NPE) ethanols containing up to 10 moles of ethylene oxide by programmed-temperature gas chromatography and also found good agreement with a theoretical Poisson distribution. Kelly and Greenwald[3] laboriously separated a *tert.*-octylphenoxy polyoxyethylene ethanol with an average EO number of 9.7 (OPE-9.7) into individual ethoxymers by conventional silica gel liquid chromatography and showed good agreement between the isolated ethoxymers and predicted Poisson distribution. In a similar vein, Mayhew and Hyatt[4] molecularly distilled NPE-6 and OPE-9.5 polyoxyethylene alkylphenols and showed that the mole ratio distributions followed Poisson distributions. Bombaugh[5], addressing chromatographic technique rather than the distribution question, compared the chromatography of Triton® X-45 and Triton® X-100 by both long column (160 ft.) and short column (4 ft.) recycle gel permeation chromatography.

High-performance liquid chromatography (HPLC) has been used more recently for characterizing surfactants[6–12]. This work was generally performed with silica gel column packing[6–10] and satisfactory resolution was shown only for adducts up to 9 or 10 EO units. A Varian Application Note[11] suggested that a bonded phase NH_2 column might be better suited for this type of separation but this particular application note also seemed to indicate loss of resolution at about 10 EO units.

Since we were most interested in examining EO distributions in the 6 to 40 range, we directed our efforts to improving the method. Some time after we had developed our method, Hayman and Parris[12] delivered a paper at the 1979 Pittsburgh Conference which reported a method with a CN column which could separate ethoxymers up to 30 units. However, we experienced a badly drifting baseline with their method, due to the gradient, for higher ethoxymer distributions and we found our method more satisfactory for quantitation purposes.

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TABLE I

SOLVENT GRADIENT CONDITIONS FOR NPE OR OPE SURFACTANTS

Solvents: A = isooctane–methylene chloride–methanol (95:5:3); B = isooctane–methylene chloride–methanol (60:40:7.5). MDC = Methylene chloride.

NPE or OPE chain length	*Time of linear gradient (min)*	*Gradient limits*	*Sample concentration*	*Injection size*
6	30	100% A to 50% A–50% B	75 mg in 20 ml MDC	15 μl
9–10	30	100% A to 50% A–50% B	75 mg in 10 ml MDC	25 μl
16	45	100% A to 100% B	75 mg in 10 ml MDC	20 μl
30–40	45	100% A to 100% B	150 mg in 10 ml MDC	25 μl

EXPERIMENTAL

Apparatus

All HPLC work was performed using two Waters Assoc. (Milford, MA, U.S.A.) M6000A pumps, a Schoeffel Model 770 variable-wavelength UV detector at 276 nm and a DuPont Zorbax-NH_2 6-μm (25 cm × 4.6 mm) analytical column and an in-house packed LiChrosorb-NH_2 10-μm guard column (5 cm × 4.6 mm) in series. The analytical column was thermostatted at 30°C by a Waters column jacket. The chromatography of a series of nonyl- and *tert.*-octylphenol polyoxyethylene surfactants was accomplished by linear gradient programming, using a Waters Assoc. Model 660 solvent programmer between various proportions of isooctane–methylene chloride–methanol (95:5:3) and isooctane–methylene chloride–methanol (60:40:7.5). All flow-rates were at 2 ml/min. The conditions for classes of OPE and NPE chain length are tabulated in Table I. Peak integrations were obtained using a Spectra-Physics Minigrator.

Chemicals

Surfactants were obtained either water-free or as aqueous solutions. Water-free samples were dissolved in methylene chloride and were analyzed directly. Aqueous solutions were handled by carefully stripping small amounts of the samples on a heated rotary evaporator. The resultant water-free samples were then weighed and dissolved in methylene chloride.

Burdick and Jackson distilled-in-glass solvents were filtered through a 0.45-μm Millipore Solvinert filter before formulating the mobile phases.

Molecularly homogeneous *p-tert.*-octylphenoxypolyethoxyethanols used as standards were prepared by Mansfield and Locke[13].

Polyethylene glycol free OPE-30 and OPE-40 surfactants were obtained from technical samples via the Weibull[14] ethyl acetate extraction procedure. One hundred grams of surfactant was dissolved in 100 ml of ethyl acetate and was extracted with three 100-ml portions of 5 *N* sodium chloride. The polyethylene glycol quantitatively passes into the water layer and the surface active portion, which is retained in the ethyl acetate layer, is obtained by evaporating off the solvent. If desired, the polyethylene glycol can be removed from the water layer with chloroform.

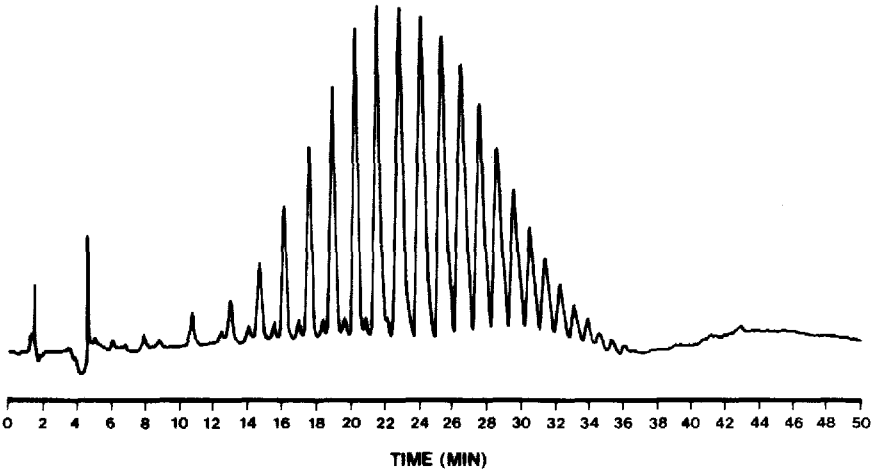

Fig. 1. Triton X-165; 45-min linear gradient, 100% A to 100% B where A = isooctane–methylene chloride–methanol (95:5:3); B = isooctane–methylene chloride–methanol (60:40:7.5); 276 nm.

Procedure

Peak areas were used to calculate the mole percent and average EO number of each ethoxymer. This was accomplished by: (1) listing all peaks areas, (2) adding all areas to find the total area, (3) calculating the area fraction (equivalent to mole

TABLE II

EO DISTRIBUTION OF TRITON X-165

EO No.	*Peak area*	*Mole fraction × 100%*	*Mole fraction × EO No.*
5	1677	0.23	0.0115
6	4613	0.63	0.038
7	5980	0.82	0.057
8	10920	1.50	0.12
9	17198	2.36	0.21
10	26677	3.66	0.37
11	37949	5.21	0.57
12	49877	6.85	0.82
13	61675	8.47	1.10
14	70896	9.74	1.36
15	75482	10.37	1.56
16	75688	10.26	1.64
17	69742	9.58	1.63
18	60879	8.36	1.50
19	50123	6.89	1.31
20	38442	5.28	1.06
21	27844	3.83	0.80
22	19332	2.66	0.58
23	12400	1.70	0.39
24	6877	0.94	0.23
25	3026	0.42	0.10
26	1448	0.20	0.05
	727745	99.96	av. EO = 15.50

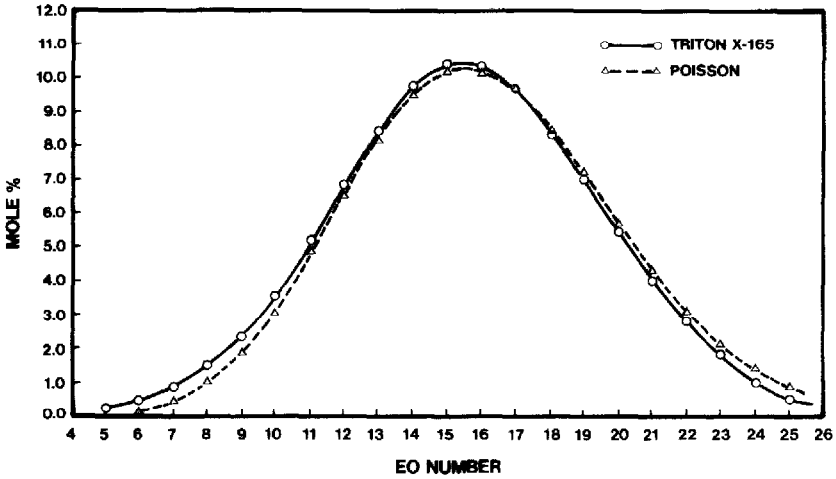

Fig. 2. HPLC distribution for Triton X-165 and Poisson distribution for OPE-16.

fraction) of each ethoxymer and (4) multiplying each mole fraction by its ethoxymer number (addition of which gives average EO number). An example is shown in Fig. 1 and Table II.

The most important aspect of this analysis is the use of a standard to identify the ethoxymer peaks. We used a single ethoxymer standard of known EO number (OPE-9).

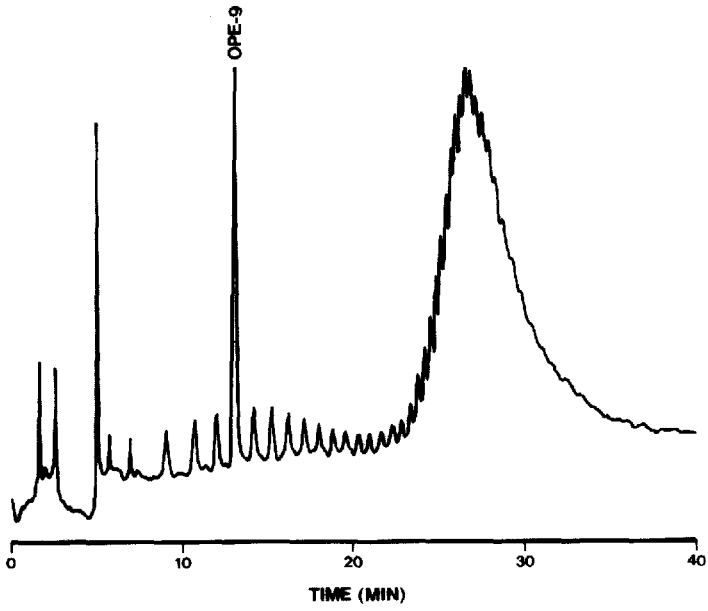

Fig. 3. OPE-40 Surfactant with OPE-9 spike; 45-min linear gradient; isooctane–methylene chloride–methanol (95:5:3) to isooctane–methylene chloride–methanol (60:40:7.5).

RESULTS AND DISCUSSION

Resolution of longer chain ethoxymers seemed to be greatly enhanced through the use of the DuPont Zorbax-NH_2 column, exceeding the performance of even ganged columns with other NH_2 packings. The consistency of long term reproducibility and resolution has been very satisfactory.

We have shown that the molar absorptivity of poly-EO substituted alkylphenols derives from the alkylphenol chromophore and is independent of EO chain length. Therefore, one can directly correlate the UV detector peak area with ethoxymer mole percent. A plot of mole % *versus* EO number for a typical Triton® X-165 (Rohm and Haas Co.), taken from Table II, is shown in Fig. 2. This agrees very well with the predicted Poisson distribution.

Although complete distributions for OPE-40 ethoxymers are difficult to obtain, due to loss of resolution at high EO number, this method is extremely useful for direct comparison between samples. The partially resolved envelope can be assigned an average EO number by counting peaks from an OPE standard to the highest peak in the envelope.

We were surprised to find that many EO-40 surfactants that we examined were closer to EO-30, usually having average EO chain lengths of 30 to 35, as in the case of Fig. 3.

Average chain length of OPE-40 surfactants, as predicted by HPLC, have been confirmed by nuclear magnetic resonance (NMR) analyses of ethyl acetate extracted

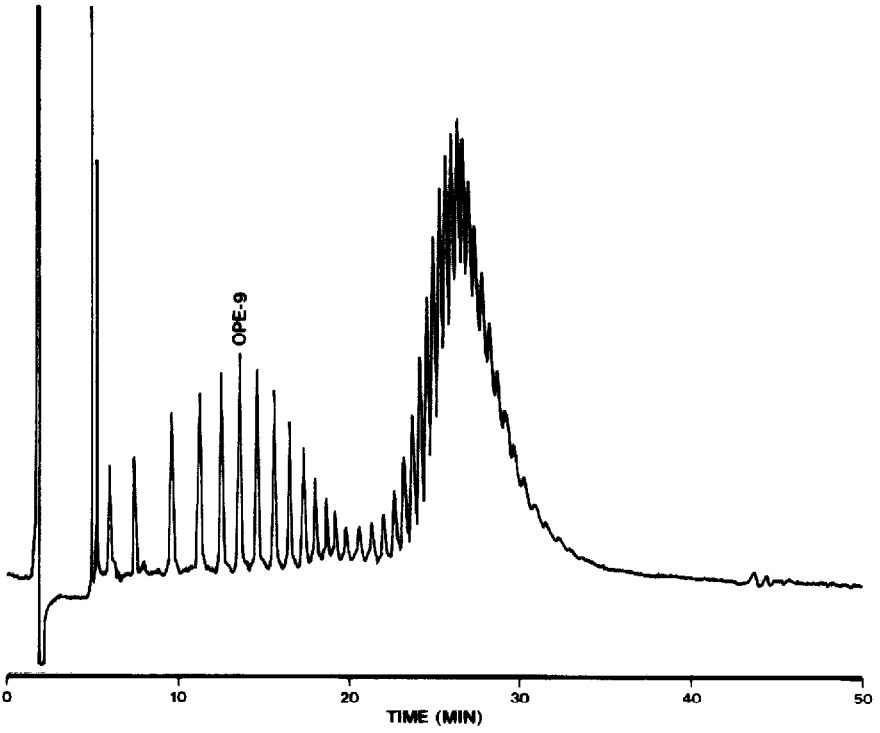

Fig. 4. Triton X-100 in OPE-40 surfactant.

samples. By extracting with ethyl acetate, the pure OPE or NPE portion can be separated from the interfering polyethylene glycol and a ratio can be obtained for the *tert.*-octyl or nonyl protons and the ethoxylate protons.

Polyethylene glycol content has also been determined by area comparison of a standard extracted sample with an unknown sample of similar ethoxymer distribution.

Lower-molecular-weight surfactants of known ethoxymer distribution can also be used as OPE (or NPE) markers for higher-molecular-weight ethoxylates. In Fig. 4 Triton X-100 (Rohm and Haas Co.) was used as a marker in an OPE-40 surfactant. This clear delineation of ethoxymer distributions is useful to clearly indicate inadvertent batch contamination of surfactants.

CONCLUSION

The improved HPLC method described here for non-ionic surfactants has proven a very useful tool for quality control and for trouble shooting. Since it has been shown that ethoxymer distribution dramatically affects the performance of the surfactant in such applications as emulsification[4] and emulsion polymerization reactions[15], it is clear that knowledge of the surfactant's ethoxymer distribution is of paramount importance. Although these surfactants are major commercial products, being found in an extremely wide spectrum of use, very little detailed characterization work to insure uniform quality has been previously reported.

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