Technical

Ethylene Oxide Oligomer Distribution in Nonionic Surfactants via High Performance Liquid Chromatography (HPLC)

M.C. ALLEN and D.E. LINDER, Research and Development Department,
Conoco Inc., Ponca City, OK

ABSTRACT

A high performance liquid chromatography (HPLC) method using adsorption columns combined with linear gradient elution has been developed for the determination of ethylene oxide (EO) distribution in nonionic surfactants. The quantitative ethoxylate adduct distribution in single-carbon-number and mixed-carbon-number primary alcohol-based samples can be obtained. The HPLC method is also applicable for determining the molar EO distributions in diverse ethylene oxide adduct compounds such as alkylphenol ethoxylates, branched alcohol ethoxylates and secondary alcohol ethoxylates. Nonionic surfactant samples containing adducts up to 25 mol have been successfully separated and the individual adducts quantitated.

INTRODUCTION

Although there has been a number of papers (1-9) on the determinations of nonionic surfactants in a variety of matrices, these methods generally determine the total nonionic surfactant content. Few methods have been developed toward characterizing these nonionic surfactant oligomers by mole (mol) of ethylene oxide.

Investigation employing thin layer chromatography (TLC) has been used to separate various oligomers of ethoxylates. Fischesser and Seymour (10) reported the separation of ca. 12 oligomers of an alkyl ethoxylate mixture by a programmed multiple development TLC procedure. Favretto et al. (11) have also used TLC for separation of slightly volatile ethoxylate oligomers. Recently, Stancher et al. (12) combined the TLC method of Favretto et al. with a gas liquid chromatographic (GLC) determination of the ethoxylate oligomers in the 15-to-18-mol adduct range.

The analysis of ethylene oxide adducts of secondary alcohols has been carried out by Puschmann (13). In his procedure, the oligomer is reacted with acetic anhydride and boron trifluoride to form an alcohol acetate and polyethylene glycol diacetate. The cleavage products were then determined by GLC.

Brüschweiler (14) developed a method for fingerprinting nonionic surfactants and emulsifiers containing a range of ethylene oxide adducts by high pressure liquid chromatography (HPLC) using an adsorption column and a complex derivatization, concentration and gradient elution scheme. Brüschweiler (14) alluded to determining distributions, but no data were presented to establish distributions and/or quantitation.

Experience in this laboratory with ethoxylate separations by TLC indicated that mixed-carbon-number alcohol ethoxylates should be separable via adsorption chromatography. A paper by Nakamura and Matsumoto (15) showed that ethoxylates of commercially available, single-carbon-number alcohols could be separated by adsorption HPLC of the acetate derivatives using a flame ionization detector.
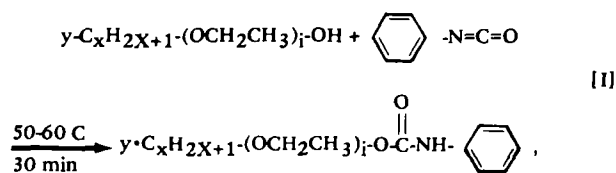
This paper describes an HPLC method using adsorption columns combined with linear gradient elution for the separation and quantitative determination of ethoxylate oligomers derived from normal, secondary and branched alcohols and alkyl phenols.

This method should also be applicable for trace level determinations of nonionic surfactants after concentration and isolation from aqueous media.

EXPERIMENTAL

Two separate, but related, adsorption HPLC techniques are used to separate the ethylene oxide adducts and to determine the ethoxylate distribution. Both require preparation of phenyl isocyanate derivatives of the alcohol ethoxylate samples for the purpose of detection by ultraviolet absorption. The following equation describes the derivatization reaction:

$$y\text{-}C_xH_{2x+1}\text{-}(OCH_2CH_3)_i\text{-}OH + \bigcirc\text{-}N=C=O$$

[1]

$$\xrightarrow[\text{30 min}]{\text{50-60 C}} y\cdot C_xH_{2x+1}\text{-}(OCH_2CH_3)_i\text{-}O\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}NH\text{-}\bigcirc,$$

where y can represent normal, secondary or branched hydrocarbon chains; x = the carbon number, normally 10 through 18, individually or in mixtures; i = the number of ethoxylate oligomers present, usually from 1 to ca. 25.

The phenyl isocyanate derivatives indicated in Scheme I are prepared using ca. 5-mg samples and 5 μL of phenyl isocyanate. The reaction is carried out at 50-60 C over a period of about 30 min. The prepared derivatives are allowed to cool to ambient temperature prior to being dissolved in 2 mL of methylene chloride containing ca. 5% 2-propanol. Suitable injection volumes are chosen to yield good response from the ultraviolet (UV) detector. The variable wavelength UV detector (Model LC-55, Perkin-Elmer, Norwalk, CT) is nominally operated at 240 nm. Two μ-Porasil (Waters Associates, Milford, MA) adsorption columns are used in tandem with a linear solvent gradient for the separation of ethoxylate oligomers by individual adducts. Other normal phase (adsorption) columns have not been used but should be expected to behave similarly with perhaps a minor solvent modification being necessary. The term "oligomer" is used in this paper for a group of individual adducts containing varying numbers of ethylene oxide units.

The first method to be described is used for the 1-through-8-mol adducts whereas the second is used for the 4-ghrough-25+ mol adducts. The results of the 2 runs are merged, yielding an overall distribution. The differences between the methods lie in the solvent system and gradients

used. Two solvent systems are required for total separation since neither will effect a complete separation by itself.

The methodology for determining the low-mol-adduct employs a solvent system of butyl chloride and 2-propanol with a starting 2-propanol concentration of 2% and running a linear gradient to 32% over a run time of 1 hr. The higher-mol-adduct method requires methylene chloride as a solvent instead of the less polar butyl chloride and a linear gradient of 3% 2-propanol to 18% 2-propanol over a run time of 1 hr. The flow rates should be between 2 mL/min and 4 mL/min. The exact rate is immaterial, but the consistency of flow is important. The separation and detection system is presently interfaced to an automatic sample injector (WISP, Waters Intelligent Sample Processor, Waters Associates, Milford, MA) and a Shimadzu Data Processor (Waters Associates, Milford, MA), allowing appropriate area integration and subsequent data processing.

After each sample has been run via both methods, the ethoxylate peak areas are tabulated and identified. Peak area identification is done by comparing elution times to those of individual adduct standards. The areas are then collated from each separation, and the areas from corresponding adducts are rationed to obtain one set of raw peak areas representing a composite separation of from 1 to 25 or more adducts. With the molecular weight (MW) of the starting alcohols and the concentration of ethylene oxide known, the average number of mol of ethylene oxide/mol of alcohol and the normalized weight percentage of such an adduct may be calculated. The following formulas show how these calculations are made:

$$v = \frac{(EO\%)(M_O)}{M(100\text{-}EO\%)}, \qquad [II]$$

where v = average ethylene oxide mol number; EO% = ethylene oxide incorporated (%); M_O = MW of starting alcohol; M = MW of ethylene oxide.

The average weight fraction is given by:

$$\overline{W}_i = \frac{M_O + iM}{M_O + vM} \, N_i, \qquad [III]$$

where M_O = MW of alcohol; M = MW of ethylene oxide; v = average ethylene oxide mol number; i = ethylene oxide unit in ethoxylate; $\overline{W}$ = average weight fraction; N = mol fraction = area fraction.

The weight percentages for each mol adduct are then normalized as shown in the following equation:

$$W_i\% = \frac{\overline{W}_i}{\displaystyle\sum_{i=1}^{n} \overline{W}_i} \times 100, \qquad [IV]$$

where $\overline{W}_i$ = normalized average %; n = total number of mol ethylene oxide.

These results are further analyzed by incorporating the percentage of free alcohol content obtained by other techniques, renormalized and plotted vs ethylene oxide unit for visual analysis.

The free alcohol derivatizes also and coelutes with the excess phenyl isocyanate and, therefore, is not directly determinable.

If one is running an unknown ethoxylate sample, the average mol EO can be determined directly from the HPLC data by a mol number weighted average of the adduct peak areas. Analysis by GLC and de-ethoxylization with subsequent GLC analysis should yield the free alcohol and alkyl distribution. From these data, one should be able to calculate the average MW of the starting alcohol. From these data, then, the weight fraction can be calculated.

RESULTS AND DISCUSSION

As stated earlier, previous work in this laboratory and in the literature (14,15) indicated the feasibility of using adsorption HPLC for the separation by individual ethoxylate adduct. The major advantage gained by using adsorption chromatography instead of reverse-phase chromatography was that the carbon number of the parent alcohol would have minimal effect on the subsequent separation by ethylene oxide unit. This was demonstrated on a mixed carbon number (C_{12} through C_{18}) commercial alcohol ethoxylate and on other, narrower-range-carbon-number mixtures. The results from these runs indicated only moderate peak broadening as a major effect from the separation of mixed-carbon-number, alcohol-based ethoxylate samples.

In order for the method to be able to produce quantitative distributions, 4 pieces of information were needed: (a) the numbering of the ethoxylate peaks (standards), (b) the responses of the molar adducts (linearity), (c) reproducibility and (d) applicability.

Ethoxylate standards were initially procured from Nikkol Chemical, Japan. Those were individual molar adducts of single-carbon-number alcohol ethoxylates. The 1-mol through 8-mol adducts of the C_{12} alcohol were obtained. This allowed the identification by retention volume of the first 8 adducts and subsequent sequential number of the 9-through-25+ adducts. This allowed us to satisfy the first of our 4 questions directly. The second question, dealing with molar responses, was also answered, both with use of these standards and real samples which were coanalyzed by GLC and HPLC techniques. Since the UV detector responds to the phenyl ring of the phenyl isocyanate and since only 1 ring/derivative molecule of alcohol ethoxylate exists, the responses should be molar, and this was true. Table I lists the results obtained from the dual analysis of 2 C_{12} alcohol ethoxylate samples by GLC and HPLC where the data shown were wt. %, using an internal standard, and the HPLC data assumed molar response and then calculated for wt. %.

Figure 1 shows the separation of a blend of the individual ethoxylate adducts achieved by the low-mol-adduct method. Figure 2 shows a similar separation for an average

TABLE I

Analysis by GLC and HPLC of Two C_{12} Alcohol Ethoxylate Samples (60% EO)

	$\overline{W}$% EO			
	Sample A		Sample B	
EO no.	GLC	HPLC	GLC	HPLC
1	0.43	0.47	1.37	2.85
2	0.73	0.84	1.91	1.93
3	1.38	1.71	2.74	2.41
4	2.53	3.11	3.56	3.90
5	4.39	4.40	4.20	4.35
6	6.77	6.56	5.24	5.54
7	9.3	9.5	6.3	6.14
8	10.9	10.9	–	8.10
9	–	12.48	–	9.44
10	–	14.48	–	9.65
11	–	10.01	–	8.80
12	–	9.40	–	7.58
13	–	6.16	–	6.45
14	–	4.21	–	5.86
15	–	2.80	–	4.88
16	–	1.55	–	4.20
17	–	0.92	–	3.21
18	–	0.44	–	2.40
19	–	–	–	1.49
20	–	–	–	0.82

9-mol C_{12} alcohol ethoxylate sample which was used in determining molar responses. Table II gives the precision data on a blend of the 1-through-8-mol adducts and Tables III and IV give similar data on 2 differing C_{12} alcohol ethoxylate samples. Four analyses for each sample were generated for statistical purposes except where noted.

Figure 3 again shows the results obtained on a mixed-carbon-number alcohol ethoxylate sample (C_{12}, C_{18}, even carbon numbers, with 70% EO). Peak broadening is the major effect on the separation of these ethoxylates of mixed-carbon-number alcohols. The small in-between peaks generally can arise from PEG adducts and, when large excesses of phenyl isocyanate are used, small amounts of double adducts of the urea type can form, which causes
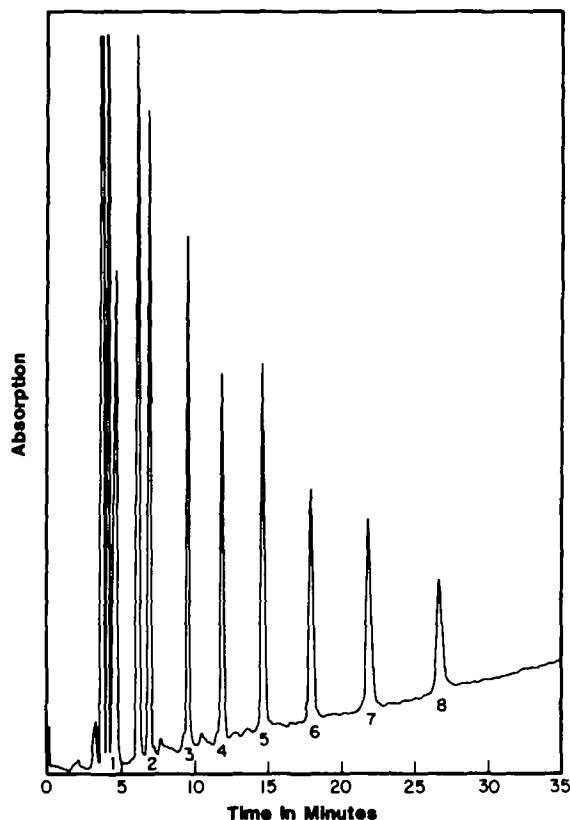
FIG. 1. Blended standard—1 through 8 mol alcohol ethoxylate adducts, low mol separation.
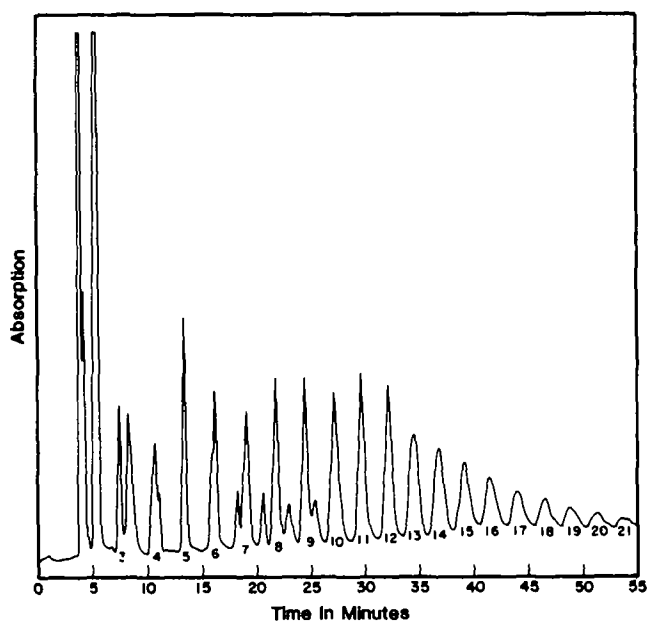
FIG. 2. Alcohol ethoxylate sample C average 9 mol adduct, high mol separation.

TABLE II

Analysis of Blended Standard C_{12}
Alcohol Low Mole Adduct Method[a] (n=4)

EO no.	$\overline{X}$ (wt. %)	Std. dev.	% Std. dev. of $\overline{X}$
1	7.00	0.30	4.4
2	5.95	0.19	3.2
3	4.39	0.07	1.6
4	3.85	0.06	1.6
5	5.08	0.05	1.0
6	3.58	0.07	2.0
7	3.96	0.26	6.6
8	2.95	0.16	5.4

[a]Appropriate peak area percent only.

TABLE III

C_{12} Alcohol Ethoxylate Sample C (60% EO, n=4)

EO no.	$\overline{X}$ (wt. %)	Std. dev.	% Std. dev. of $\overline{X}$
1	0.98	0.13	13.2
2	1.56	0.21	13.3
3	2.87	0.12	4.2
4	3.78	0.16	4.1
5	4.60	0.07	1.5
6	5.72	0.22	3.9
7	7.09	0.24	3.4
8	7.76	0.24	3.1
9	7.94	0.64	8.0
10	8.60	0.17	2.1
11	8.57	0.14	1.6
12	8.02	0.08	1.0
13	7.18	0.36	5.0
14	6.44	0.35	5.5
15	5.50	0.20	3.5
16	4.32	0.25	5.8
17	3.04	0.35	11.5
18[a]	2.49	0.05	1.9
19[a]	2.01	0.11	5.4
20[a]	1.57	0.12	8.5

[a]Three values only.

TABLE IV

C_{12} Alcohol Ethoxylate Sample D (60% EO, n=4)

EO no.	$\overline{X}$ (wt. %)	Std. dev.	% Std. dev. of $\overline{X}$
1	0.38	0.013	3.4
2	0.81	0.17	21.0
3	1.42	0.09	6.7
4	2.41	0.04	1.9
5	4.12	0.17	4.2
6	6.27	0.14	2.3
7	8.53	0.16	1.9
8	10.9	0.49	4.5
9	11.7	0.4	3.4
10	12.3	0.25	2.0
11	11.2	0.53	4.8
12	9.9	0.78	7.9
13	7.2	0.40	5.6
14	5.4	0.38	7.0
15	3.5	0.57	16.0
16	2.2	0.22	10.0
17	0.8	0.44	55.0

differences in elution times and greatly increased absorptivities beyond one phenyl ring.

Figure 4 shows the results obtained on a nonylphenol ethoxylate (high-mol separation) whereas Figure 5 depicts similar information obtained on a secondary alcohol
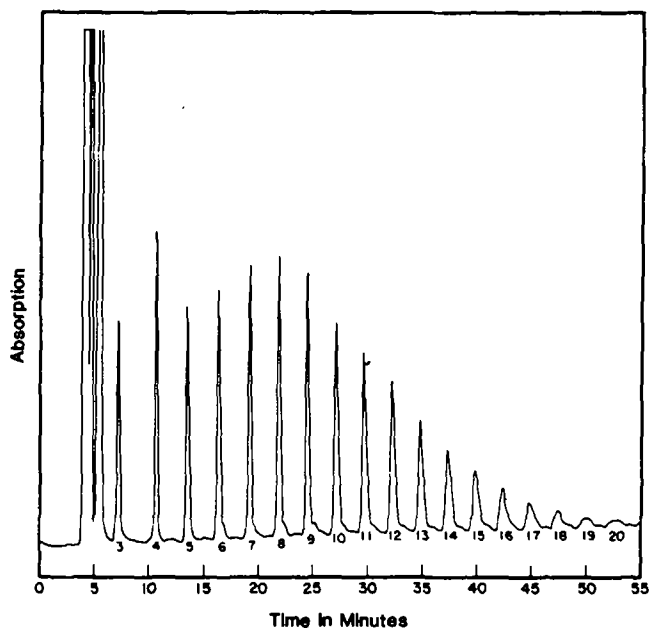

FIG. 3. High mol separation of a mixed carbon number alcohol ethoxylate (C_{12}-C_{18}, 70% EO).
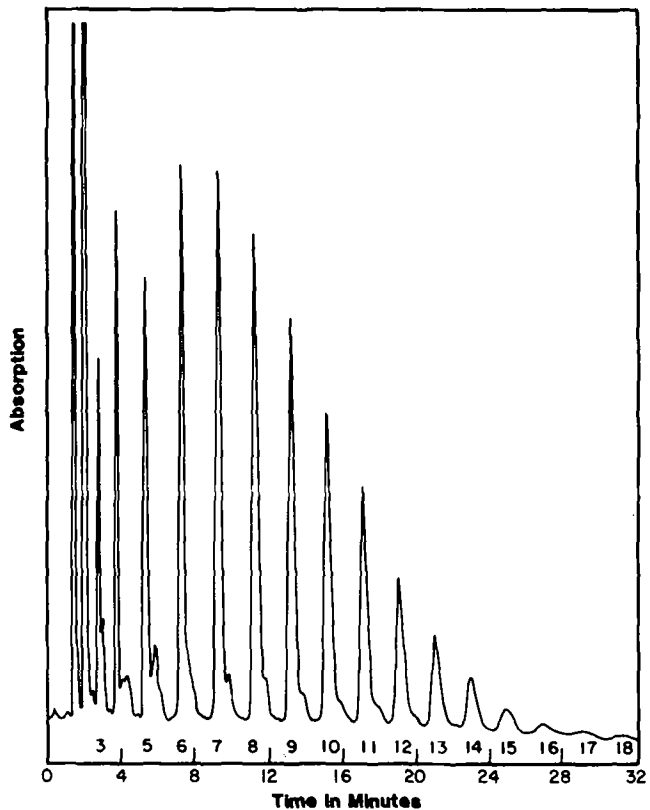
ethoxylate (C_{11} through C_{15}).

Selected alcohol ethoxylate samples were examined by these techniques. Other nonionics examined, but not illustrated, included branched-alcohol-based ethoxylates. The applicability of this HPLC technology has been shown.

Each of the alcohol ethoxylates was sampled 3 separate times and 3 separate derivatization reactions were performed. Each of these samples was then run for low-mol- and high-mol-adduct separations. The analyses were performed over an extended period of time interspersed with other samples. These experiments were designed in this manner to insure that these statistical samples would be exposed to the same operational conditions and handling as regular, one-shot samples. This provided statistics on what would be realistically expected on routine runs. No special handling or care was taken to insure improved results beyond those normally performed. Thus, the data reflect all systematic and random errors which might occur.

Table V gives the results from this statistical study whereas Table VI gives results obtained on a variety of other nonionic ethoxylates. These were examined on a once-only basis.

Figures 6 through 9 depict graphically the distribution determined from the samples given in Tables I, III and IV. The distribution of the samples listed in Table V is given in Figures 10 through 13 whereas those in Table VI are given in Figures 14 through 17. The data on these few samples selected from the large number of samples examined and those still undergoing examination illustrate some of the information that can be obtained about EO distributions from ethoxylate samples using HPLC. This methodology is also being applied to the problem of determining trace amounts of nonionic surfactants in environmental waters.
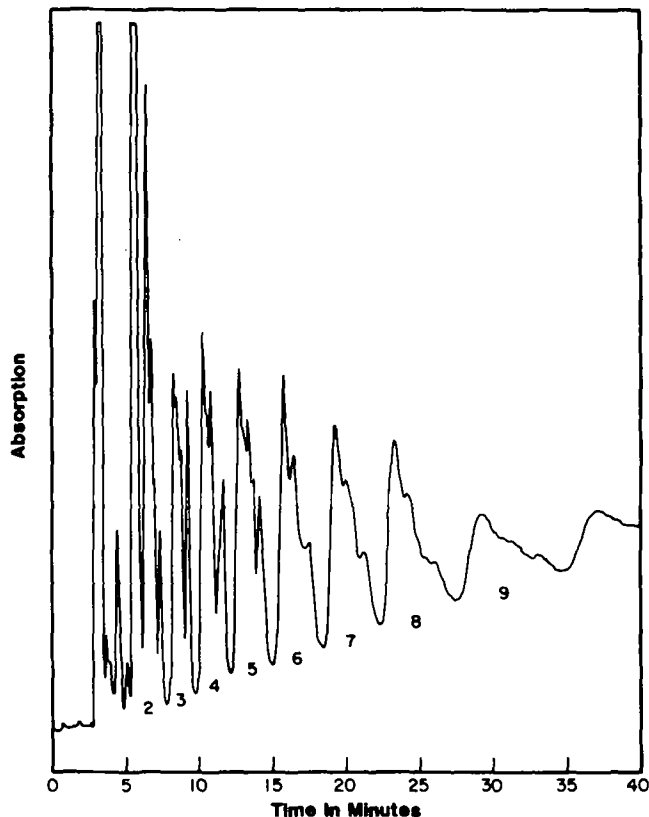

FIG. 4. High mol separation of a nonyl phenol ethoxylate, average 10.5 mol adduct.

FIG. 5. Low mol separation of a secondary alcohol ethoxylate, average 7 mol adduct.

TABLE V

EO Distribution (W̄%) and Statistical Analysis of Linear Alcohol Ethoxylates (n=4)

Alcohol carbon range % EO EO no.	12-14 60		12-14 40		10-12 60		16-18 65	
	$\overline{X}$	%SD/$\overline{X}$	$\overline{X}$	%SD/$\overline{X}$	$\overline{X}$	%SD/$\overline{X}$	$\overline{X}$	%SD/$\overline{X}$
1	2.54	4.1	14.45	4.9	5.11	6.9	1.50	14.3
2	3.69	6.0	12.86	3.2	6.50	1.5	2.00	11.6
3	4.56	0.8	13.78	4.8	7.88	0.6	2.23	4.7
4	5.75	2.3	12.13	1.5	8.97	7.2	2.82	8.0
5	7.01	3.6	10.74	0.8	10.01	1.5	3.34	5.8
6	7.51	1.2	8.71	1.9	9.84	0.8	4.33	8.4
7	8.42	2.7	7.43	1.1	9.84	0.4	5.00	2.0
8	8.80	1.3	6.02	1.5	9.27	0.5	5.90	4.5
9	8.61	2.2	4.60	4.5	8.35	0.8	6.61	5.6
10	8.28	3.7	3.54	3.0	7.13	1.9	7.08	1.5
11	7.55	3.2	2.53	6.7	5.76	1.2	7.46	3.3
12	6.56	1.7	1.68	3.1	4.40	0.9	7.69	2.5
13	5.41	2.2	0.85	25.8	3.26	9.2	7.82	1.7
14	4.38	6.3	0.66	15.1	2.00	4.2	7.54	1.8
15	3.49	7.5	–	–	1.33	2.0	6.84	1.8
16	2.62	11.8	–	–	1.78	8.0	6.08	1.7
17	2.05	11.9	–	–	0.23	41.6	5.08	0.4
18	1.40	10.2	–	–	–	–	4.04	0.9
19	0.89	10.7	–	–	–	–	3.10	3.0
20	0.56	10.2	–	–	–	–	2.31	7.1
21	–	–	–	–	–	–	1.46	4.0

TABLE VI

EO Distribution (W̄%) of Miscellaneous Nonionics

Average mol EO EO no.	7 Oxo alcohol ethoxylate (A)	10.5 Nonylphenol ethoxylate	7 Secondary alcohol ethoxylate	7 Oxo alcohol ethoxylate (B)
1	2.44	0.04	1.09	1.11
2	1.64	0.44	6.56	2.56
3	4.36	2.61	8.45	4.07
4	6.15	4.58	10.83	5.54
5	8.93	6.63	10.47	8.00
6	8.40	9.33	11.44	7.56
7	9.27	10.43	11.88	8.46
8	9.40	11.68	11.03	9.02
9	9.16	12.57	9.70	9.66
10	8.55	11.76	7.63	9.19
11	7.53	9.83	5.80	8.70
12	6.20	7.63	3.14	7.44
13	4.89	5.34	1.50	5.96
14	3.57	3.34	0.41	4.82
15	2.75	1.86	–	2.98
16	2.05	0.82	–	2.08
17	1.55	0.76	–	1.41
18	0.62	0.35	–	0.95
19	–	–	–	0.39
20	–	–	–	–

REFERENCES

1. SDA Scientific and Technical Report No. 6, "The Status Testing of Nonionic Surfactants," October 1969.
2. Wickbold, R., Tenside Deterg. 9:173-177 (1972).
3. Wickbold, R., Ibid. 10:179-182 (1973).
4. Wurzschmitt, B., Z. Anal. Chem. 130:105-183 (1950).
5. Brown, E.G., and T.J. Hayes, Analyst 80:755 (1955).
6. Greff, R.A., E.A. Setzkorn and W.D. Leslie, JAOCS 42:180 (1965).
7. Crabb, N.T., and H.F. Persinger, Ibid. 41:752 (1964).
8. Burtschell, R.H., Ibid. 43:366 (1966).
9. Linhart, K., Tenside Deterg. 9:241-259 (1972).
10. Fischesser, G.J., and M.D. Seymour, "The Determination of Alkyl Ethoxylate Mixtures by Programmed Multiple Develop-
ment Thin-Layer Chromatography," presented at the 27th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, paper no. 238, March 1976.
11. Favretto, L., G.P. Marletta and I.F. Gabrielli, J. Chromatogr. 46:255 (1970).
12. Stancher, B., I.F. Gabrielli and L. Favretto, Ibid. 111:459 (1975).
13. Puschmann, H., Tenside Deterg. 5:207-210 (1968).
14. Brüschweiler, H., Mitt. Geb. Lebensmittelunters. Hyg. 68: 46-63 (1977).
15. Nakamura, T., and O. Matsumoto, J. Chem. Soc. Jpn. 8:1432 (1975).
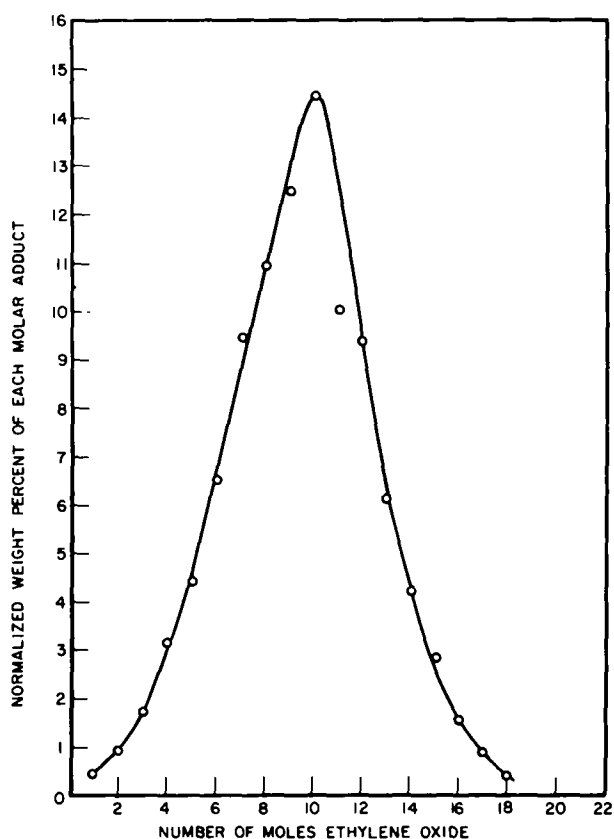
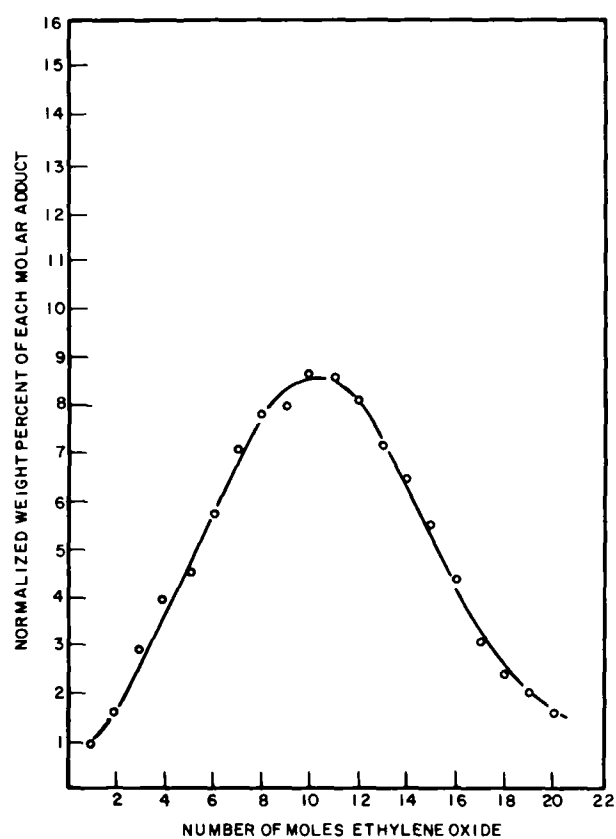FIG. 6. Distribution of a C_{12} alcohol ethoxylate sample A (60% EO).

FIG. 8. Distribution of a C_{12} alcohol ethoxylate sample C (60% EO).
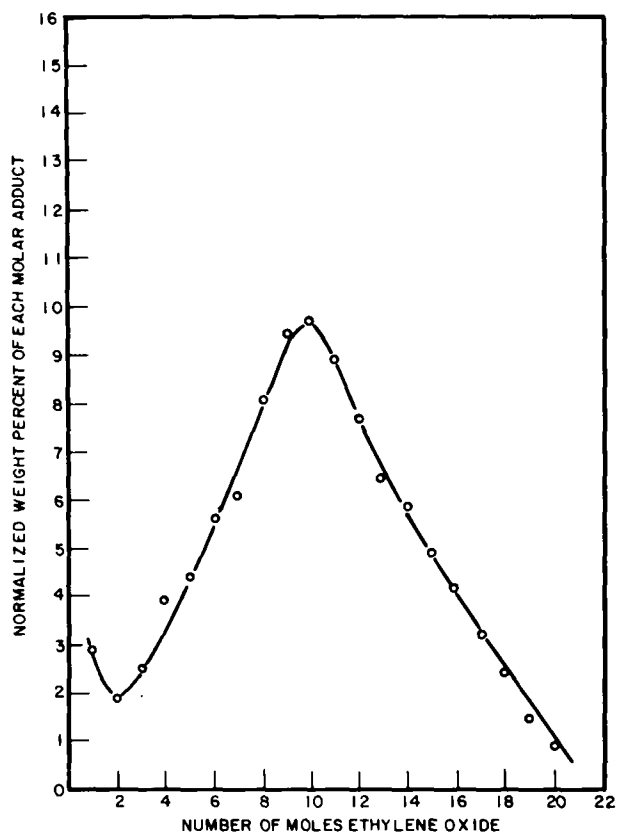
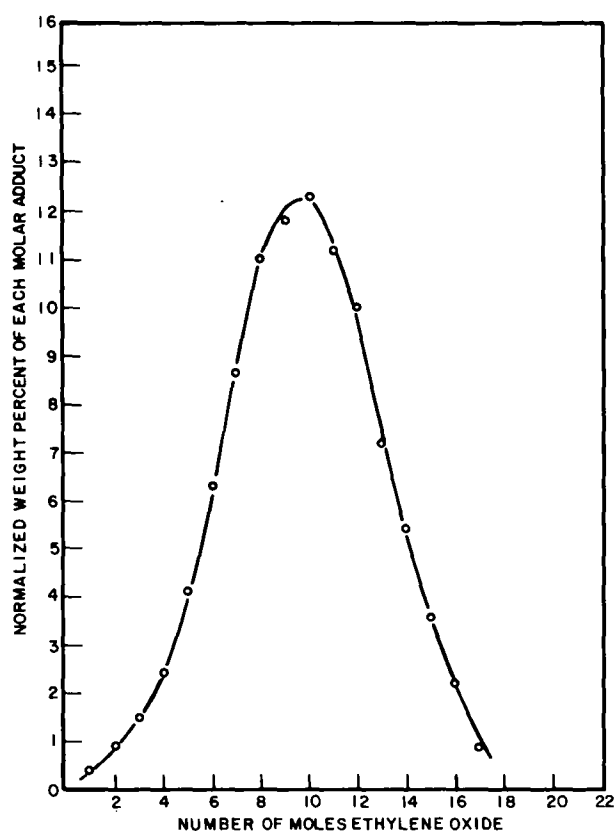FIG. 7. Distribution of a C_{12} alcohol ethoxylate sample B (60% EO).

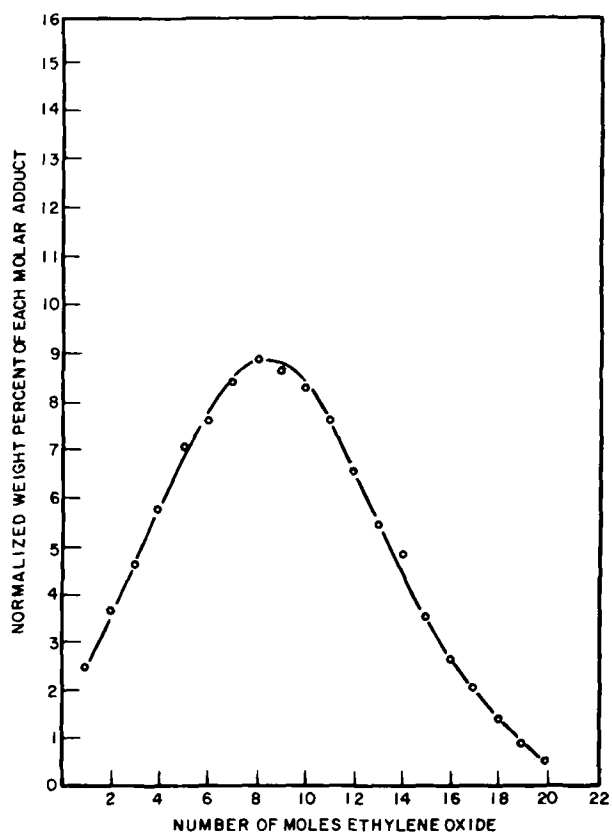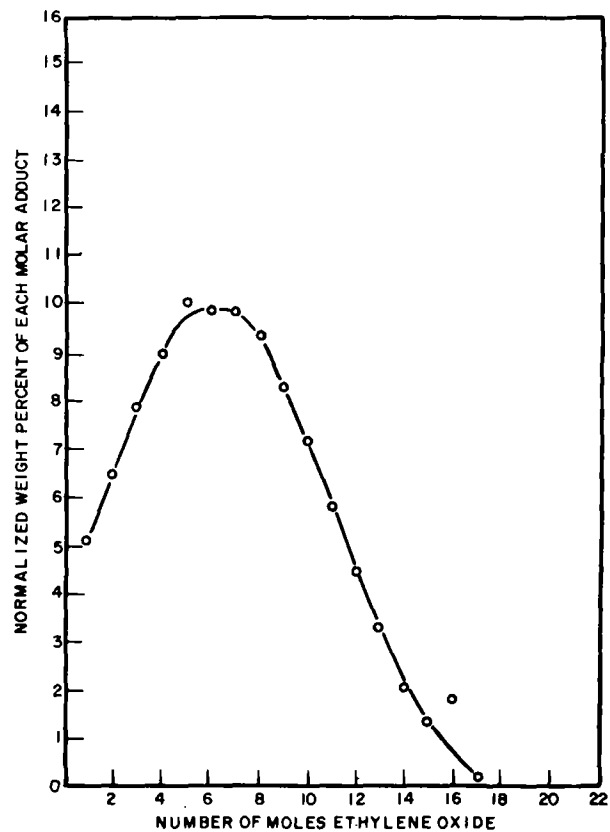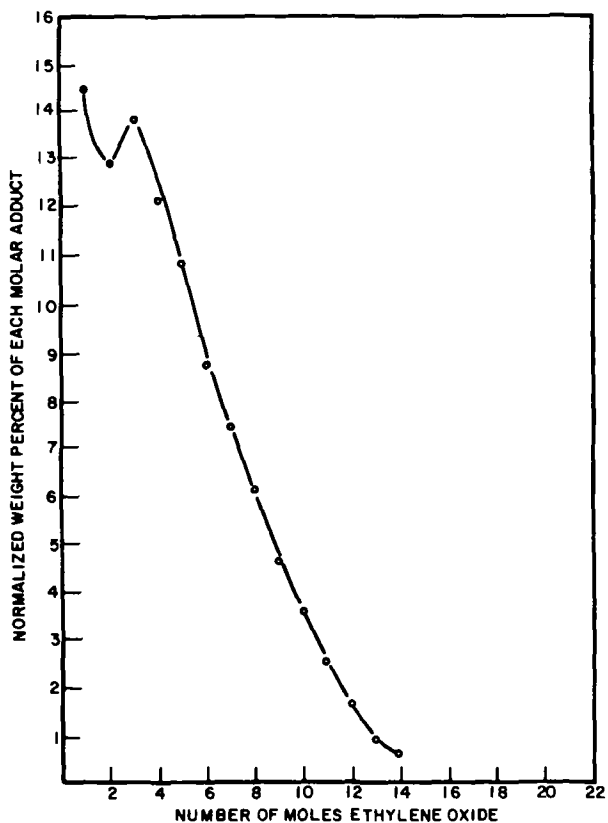FIG. 9. Distribution of a C_{12} alcohol ethoxylate sample D (60% EO).

FIG. 10. Distribution of a synthetic linear alcohol ethoxylate (C_{12}-C_{14}, 60% EO).

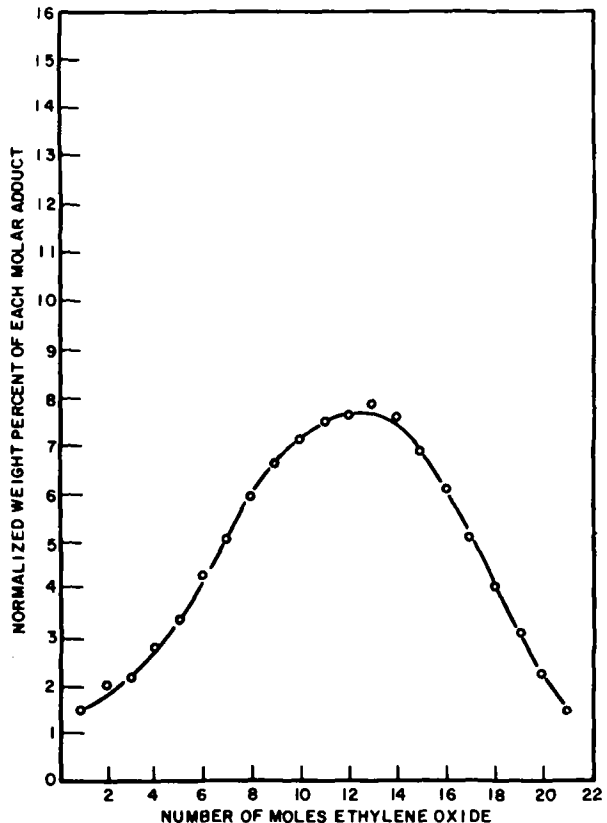FIG. 12. Distribution of a synthetic linear alcohol ethoxylate (C_{10}-$_{12}$, 60% EO).

FIG. 11. Distribution of a synthetic linear alcohol ethoxylate (C_{12}-C_{14}, 40% EO).

FIG. 13. Distribution of a synthetic linear alcohol ethoxylate (C_{16}-$_{18}$, 65% EO).
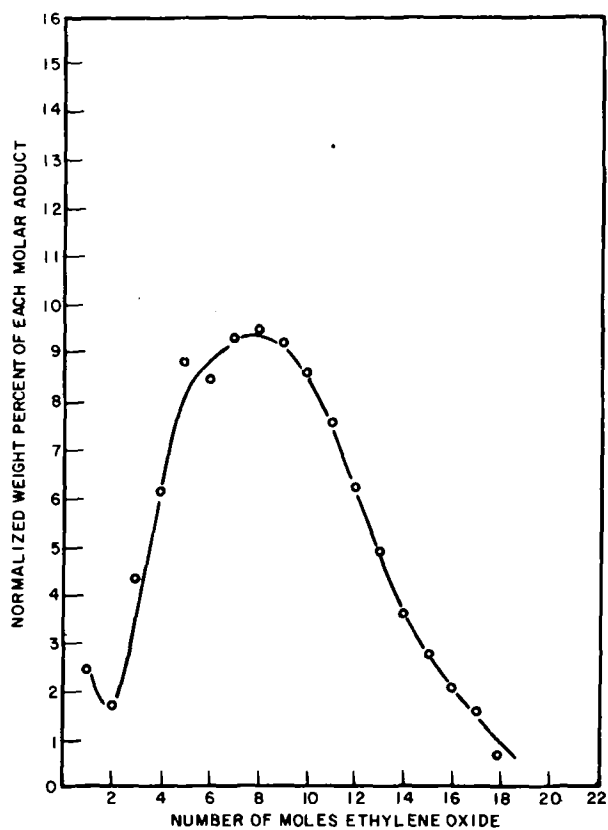
FIG. 14. Distribution of an oxo alcohol ethoxylate (A) average 7 mol adduct.
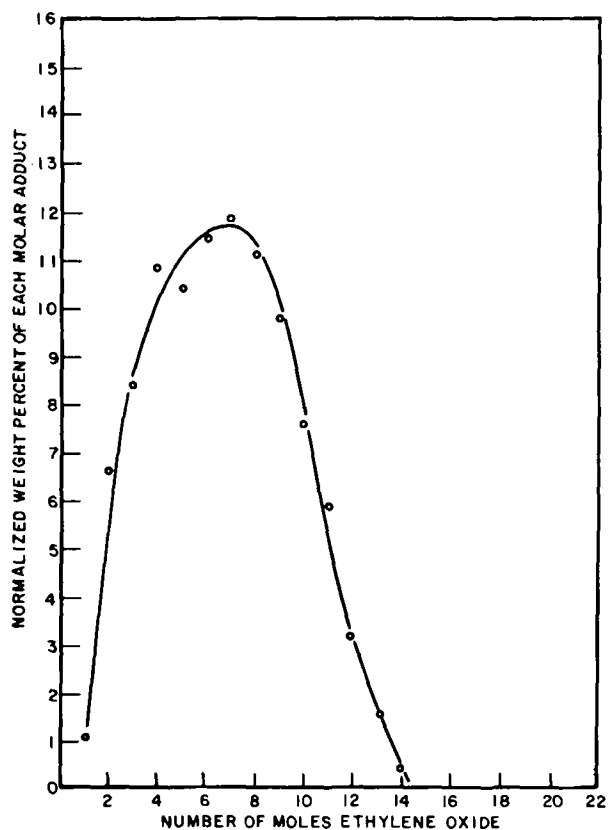
FIG. 16. Distribution of a secondary alcohol ethoxylate average 7 mol adduct.
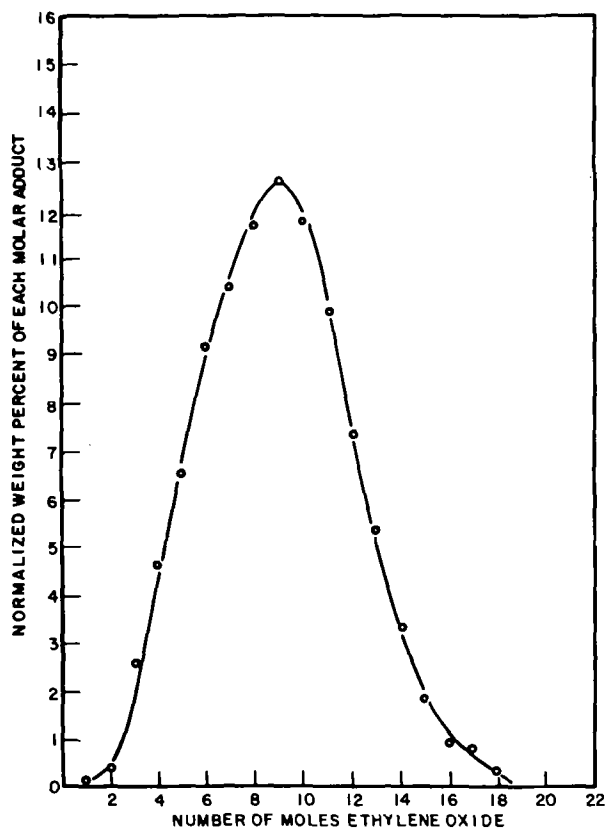

FIG. 15. Distribution of a nonyl phenol ethoxylate average 10.5 mol adduct.
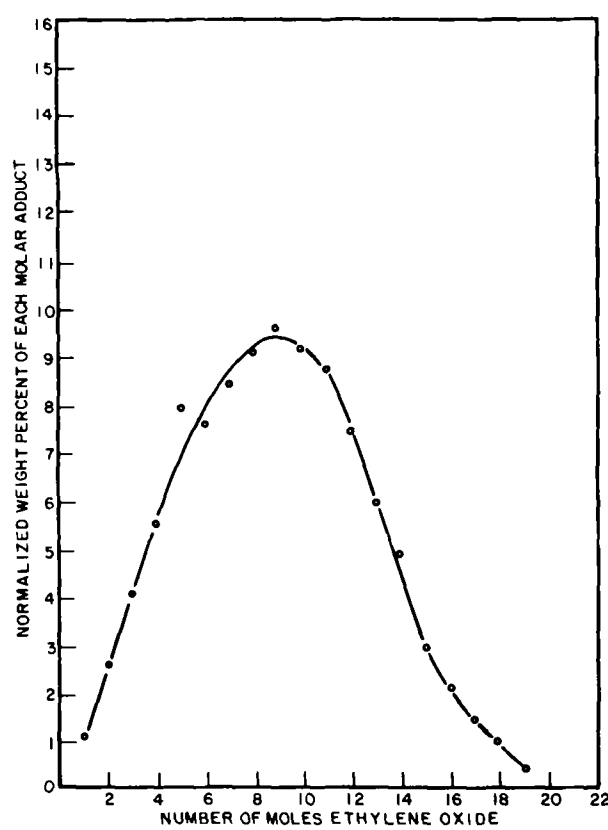

FIG. 17. Distribution of an oxo alcohol ethoxylate average 7 mol adduct.