SHORT COMMUNICATION

Quantitative Determination of Ethylene Oxide Oligomer Distribution in Ethoxylated Alkylphenol Carboxymethyl Ether Salts by Thin-Layer Chromatography

Jiang Yang*, **Lufang Zhang** and **Xiangrong Li**
Department of Applied Chemistry, University of Petroleum of China, Beijing, 100083, China

A two-dimensional thin-layer chromatographic (TLC) method was used to separate a mixture of ethoxylated alkylphenol carboxymethyl ether salts and unconverted ethoxylated alkylphenol ether with the first eluent, which was then developed at right angles with EtOAc/HOAc/H_2O as the second eluent to resolve the individual ethylene oxide oligomer adducts. Scanning densitometry was used for quantitation. The surfactant's degree of conversion, average ethoxylate number and its distribution were simultaneously determined on a single TLC plate.

KEY WORDS: Ethoxylated alkyphenol carboxymethyl ether salts, oligomer distribution, thin-layer chromatography.

In the presence of high concentrations of alkali and alkaline earth salts, ethoxylated alkylphenol carboxymethyl ether salts [APC; C_nH_{2n+1}-C_6H_4O-(CH_2CH_2O)n-CH_2COOM] can be used for surfactant flooding processes (1). APC may also be used in cosmetic products. Ethoxylated alcohols/ethylene oxide (EO) alcohol sulfates are used extensively in household products, such as laundry and dishwashing detergents. The physical and chemical properties of the resulting surfactants are strongly dependent on the distribution of EO chains (2). For determining the composition of the phases that occur during the flooding process, as well as for product control, knowledge of the distribution of EO chains is important. This characterization permits the determination of changes in product composition and the control of effectiveness.

Several techniques have been developed to determine the EO distribution of surfactants. The use of gas chromatographic methods is restricted to volatile derivatives in the determination of the distribution of EO chains (3). For determination of the EO chain distribution of the less-volatile higher members, one must resort to liquid–solid chromatography. Among these, high-performance liquid chromatographic (HPLC) methods seem to be inconvenient for routine work because the ultraviolet detector normally used in HPLC is limited to surfactants with a phenyl ring. Other surfactants that contain an EO chain but without the phenyl ring need chemical modification to be analyzed without other detectors (4,5). Thin-layer chromatographic (TLC) methods are preferred because they are simple, inexpensive and have high separation efficiency. Also, preseparation or derivatization of the sample is usually unnecessary. In the synthesis of APC, the total amount of product has been determined by Kunkel (6) by TLC. However, the determination of APC's degree of conversion and its EO chain distribution by TLC have not yet been reported.

In this paper, the degree of APC's conversion and its EO chain distribution are determined by two-dimensional TLC with verification by HPLC.

EXPERIMENTAL PROCEDURES

Apparatus. A Shimadzu Model CS-930 densitometer (Kyoto, Japan) was used in conjunction with the CCS-2 program (Shimadzu) to plot the shape of the scanned spots.

Materials. APC-n samples (n = 2, 6, 10, where n was the average number of EO chains) were synthesized and purified (n = 2) from ethoxylated nonylphenol ether (Sanyo Chemicals Co., Tokyo, Japan) in our laboratory. Molecularly homogeneous surfactant (APC-3), used as standard, was isolated by prep TLC in our lab, and its molecular weight was verified by field desorption–mass spectrometry (FD–MS). The purity was found by HPLC to be in excess of 98.0%. High-performance TLC (silica) plates, obtained from Qingdao Oceanic Chemicals Co. (Qingdao, China), were activated at 110°C for 1 h before use. Other reagents were of extra pure grade and were used without further purification.

Procedures. A sample of APC, 2–3 μL at 5–10% (wt/vol) in ethanol solution was spotted with a microsyringe 1.5 cm from the bottom and 2 cm from the left edge of a 20 × 10 cm silica-gel plate. The spot should be no larger than 2 mm in diameter. The first eluent (I) of $CHCl_3/CH_3OH/n$-C_4H_9OH/0.1N ethylenediamine tetraacetic acid (EDTA)/0.1N H_2SO_4 (16.25:6.5:5:0.7:0.4, vol/vol) was added into the developing tank with eluent height between 0.5 and 0.8 cm. The plate was developed to a distance of 8 cm by the ascending technique in the tank under a vaporsaturated atmosphere. The plate was then reactivated, and 2 μL of 5–10% (wt/vol) standard homogeneous APC-3 was then spotted on the plate between the original and developed spotted points. The plate was then perpendicularly developed for a distance of 170 cm, with EtOAc/HOAc/H_2O as the second eluent (II) (the proportions were different according to the n value in APC-n). Spots were visualized by exposure to iodine vapor. The unknown APC-n can therefore be qualitatively identified by comparing R_f values with the standard homogeneous APCs. An example of the developed spots of APC-10 is shown in Figure 1. After the spots were visualized by iodine vapor, excess iodine was evaporated from the TLC plate. The spots were directly scanned by the two wavelength-zigzag scan mode at wavelengths of λ(sample) = 282 nm and λ(ref) = 255 nm. The shape of scanned spots was plotted with the CCS-2 program after scanning. APC's degree of conversion and its EO chain distribution were simultaneously determined by scanning the spots of the first- and second-dimensional developments, respectively.

RESULTS AND DISCUSSION

The choice of development mode and developing solvent. The route used to synthesize APC follows:

---

*To whom correspondence should be addressed at Chemistry Department, University of Missouri-Rolla, Rolla, MO 65401.

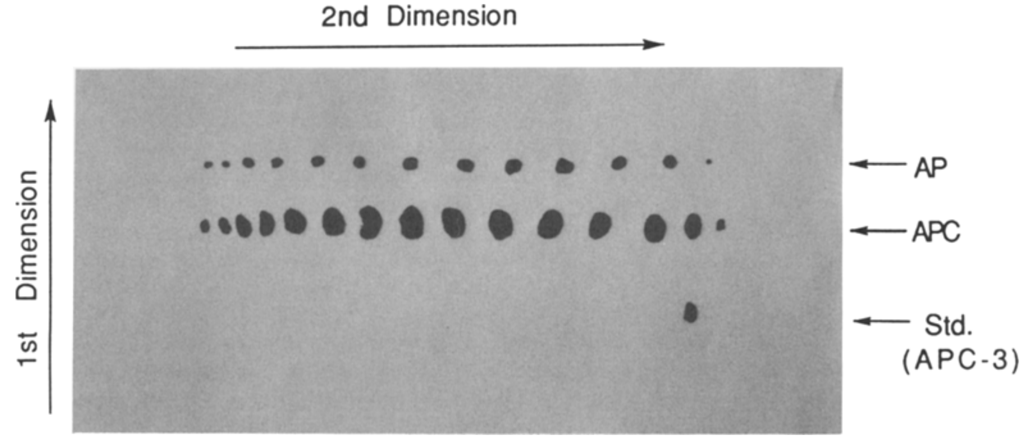

FIG. 1. Thin-layer chromatography fractionated spot distribution of ethoxylates in alkylphenol carboxymethyl (APC)-10. Eluent (I): $CHCl_3/CH_3OH/n\text{-}C_4H_9OH$/0.1N ethylenediaminetetraacetic acid/0.1N H_2SO_4 (16.25:6.5:5:0.7:0.4, vol/vol). Eluent (II): $EtOAc/HOAc/H_2O$ (9.5/2/2, vol/vol). AP, alkylphenol.

$$C_nH_{2n+1}\text{-}C_6H_4\text{-}O\text{-}(CH_2CH_2O)_nH(AP) + ClCH_2COOH \xrightarrow{NaOH}$$

$$\rightarrow C_nH_{2n+1}\text{-}C_6H_4\text{-}O\text{-}(CH_2CH_2O)_n\text{-}CH_2COONa\ (APC)$$

The EO chain distribution of unconverted ethoxylated alkylphenol (AP) was also evident under the separation conditions employed for APC. To eliminate AP's interference from the determination of APC's EO distribution, two-dimensional TLC development was used to separate AP and APC. The first-dimensional development was used to separate the APC and AP with respect of their different functional groups. The $CHCl_3/CH_3OH$ (80:20, vol/vol) eluent, proposed by Kunkel (6) to separate AP and APC, tended to streak in our experiment. Eluent (I) was suitable for the separation of AP and APC with the addition of acid and EDTA acid to the eluent. The EO distributions of the APC were then separated by the perpendicular second development of the plate. With reference to the eluent used to separate AP into its EO distribution (7), eluent (II) as described above was used in which the ratio of acetic acid and water was increased compared with eluent used in the corresponding AP with regard to the structural differences between APC and AP.

Quantitation. APC with a phenyl ring has a strong absorption in the ultraviolet region while the TLC plate has a strong reflection (8). Measurement by reflected mode has a significant advantage because it creates a steady baseline and optimum sensitivity. The iodine was used to visualize the TLC plate and locate the spots, followed by evaporation of the iodine. The scan mode with large signal/noise value and dual wavelength reflection was chosen. Two wavelengths were chosen, at the maximum reflected absorption peak at 282 nm and minimum reflected absorption peak at 255 nm. The linearization coefficient was chosen as SX3, the same as for E. Merck (Darmstadt, Germany) silica plates (9).

TABLE 1

A Comparison of Alkylphenol Carboxymethyl's (APC) Degree of Conversion Determined by TLC and Titration Technique

Surfactants (w/w)		TLC (%) (w/w)	Titration (%)
APC-2	1[a]	100	99.8
	2[a]	98.0	
APC-6	1	71.3	72.1
	2	70.1	
APC-10	1	67.5	67.4
	2	65.1	

[a] The 1 and 2 are duplicate analysis of the same sample by thin-layer chromatography (TLC). Molecular weight of surfactant used has been correlated by high-performance liquid chromatography (10).

Table 1 shows the APC's degree of conversion determined by scanning the spots of the first-dimensional development in comparison with results obtained by titrating with a standard base solution. A good correlation has been obtained between the results of the two techniques. Figure 2 shows an example of the APC-10's EO

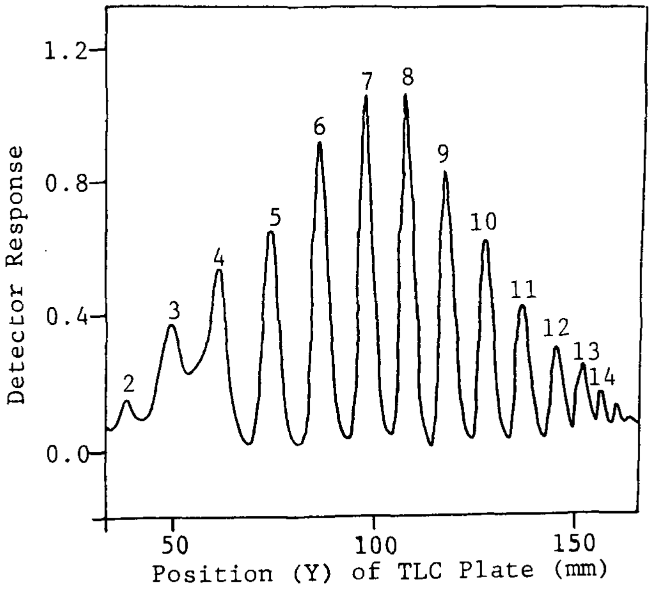

FIG. 2. Thin-layer chromatography (TLC) chromatogram of ethoxylate distribution in APC-10 (number on top of the chromatogram corresponds to ethoxylate number of separated APC). See Figure 1 for abbreviation.

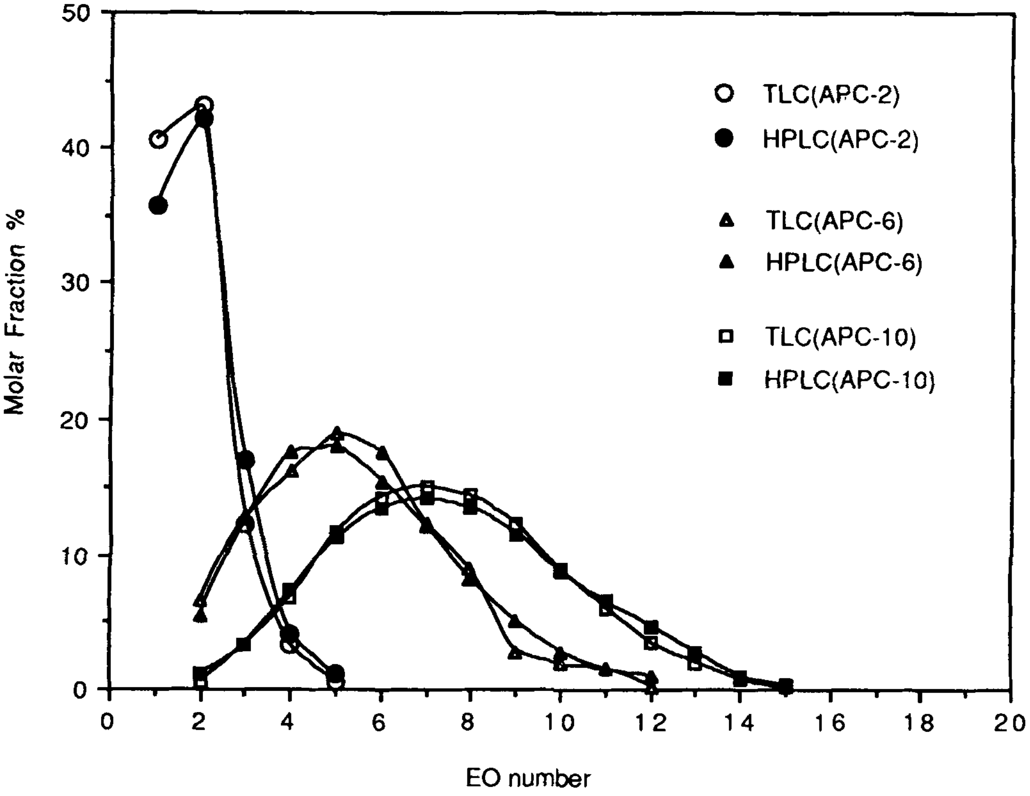

FIG. 3. The comparison of ethoxylate, distributions in APC series by high-performance liquid chromatography (HPLC) and thin-layer chromatography (TLC) based on the average values of triplicate analyses. EO, ethylene oxide; see Figure 1 for abbreviation.

distribution spots of the second-dimensional development scanned by densitometry. The relative standard deviations for the major oligomer by TLC (n = 1–2 for APC-2, n = 3–7 for APC-6 and n = 5–10 for APC-10) ranged from 1 to 17%, based on triplicate analyses. The largest deviations were found for the smallest and largest oligomers. These derivations can be attributed to their low abundance and broadening of the spots at the front edge of the TLC plate.

The EO distributions of APC were also verified by HPLC according to the method of Schuhbauer (10). Figure 3 shows the comparison of the EO distributions of APC determined by TLC and HPLC. Good agreement was found between these two techniques.

In conclusion, the EO distribution of carboxylated anionic surfactants with EO chains can be separated by two-dimensional TLC and quantitated with scanning densitometry. This method can be applied to numerous similar anionic EO surfactants.

REFERENCES

1. Akstinat, M.H., *Proceedings of Third European Symposium on Enhanced Oil Recovery*, Bournemouth, United Kingdom, 1981, p. 43.
2. Crook, E.H., and D.B. Fordyce, *J. Am. Oil Chem. Soc. 41*:231 (1964).
3. Favretto, L., and B. Stancher, *J. Chromatogr. 108*:183 (1975).
4. Huber, J.F.K., F.F.M. Kolder and J.M. Miller, *Anal. Chem. 44*:105 (1972).
5. Nozawa, A., and T. Ohnuma, *J. Chromatogr. 187*:261(1980).
6. Kunkel, E., *Tenside Detergents 17*:10 (1980).
7. Favretto, L., *Ann. Chim. 62*:478 (1972).
8. Zlatkis, A., and R.E. Kaiser, *High-Performance Thin-Layer Chromatography*, Elsevier Scientific Publishing Company, Amsterdam, 1977.
9. Yamamoto, H., *J. Chromatogr. 116*:29 (1976).
10. Schuhbauer , W., Second European Symposium on Enhanced Oil Recovery, Paris, 1982.

[Received March 10, 1993; accepted September 5, 1993]